CHEMICAL PULPING AND BLEACHING

ANNUAL PROGRAM REVIEW

SLIDE MATERIAL

MARCH 20, 1996

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March 20, 1996

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CHEMICAL PULPING AND BLEACHING

March 20, 1996 Agenda

ANNUAL PROGRAM REVIEW

8:00	Introduction/Committee Assignments	
8:10	Chemical Fundamentals of Bleaching (Project F015/Thesis Research)	
	Ozone Bleaching	Lucy Sonnenberg
	Biobleaching/High Efficiency Peroxide Bleaching	Art Ragauskas
	Organosolv Bleaching	Brian Brogdon
9:30	Environmentally Compatible Production of Bleached Chemical Pulp (Project F013)	
	Bleachability/Rapid D_0 Bleaching	Tom McDonough
10:15	Break	
10:30	Closed Mill Operations (Project F017)	
	Impact and Control of NPE's	Pat Byrant
	Novel Methods of Metals Removal - Iron	Alan Rudie
11:30	Pulping Studies (Project 3661/Thesis Research)	
	Catalysts-from-Lignin	Don Dimmel
	Characterization of Residual Lignins	Peter Froass
12:00	Adjourn	

PAC MEETING

1:00	Discussion of Projects/Future Directions	Paul Wollwage
5:00	Adjourn	

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* The dates in ( ) indicate the final year of the appointment. Revised 3/11/96

Project: F015 Fundamentals of Bleaching Chemistry

Fundamentals of Ozone Bleaching

L. B. Sonnenberg

C. E. Courchene

Purpose

- Minimize potential environmental impact of bleaching by improving TCF, ECF sequences
- Optimize efficiency and selectivity of ozone bleaching

Benefit

- Maximize ozone selectivity for specific processes
- Understand fundamental reasons for observed bleaching behavior
- Find factors that control lignin removal and carbohydrate deterioration for application to various processes throughout the industry

Related Work

- F013, Environmentally Compatible Bleaching
- F015, Oxygen-based Bleaching

General Approach

- Find pulping, delignification, and bleaching sequences that maximize lignin removal and minimize carbohydrate degradation
- Characterize pulp and dissolved byproducts; relate chemistry to bleaching behavior and paper properties

Prior Results

- Efficiency and selectivity of ozone bleaching depends on prior delignification methods
- Moderate oxygen delignification enhances ozone selectivity

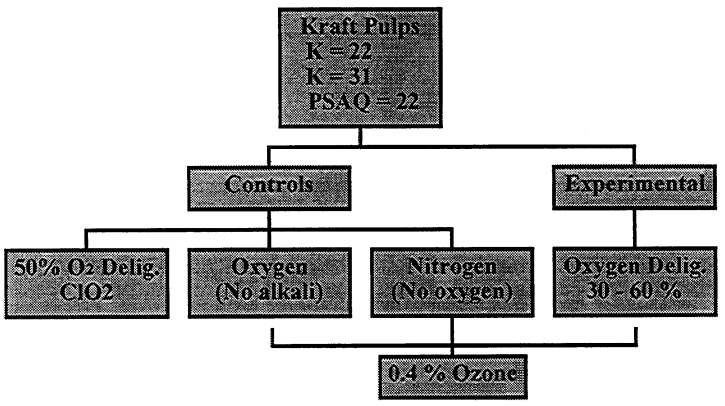
Prior Results

- Ozone produces a high proportion of small, acidic, soluble fragments at low ozone charges.
- However, ozone produces dissolved fragments with a more uniform molecular weight distribution than oxygen, which produces more low molecular weight compounds.
- Oxygen delignification prior to ozonation causes ozone to produce smaller dissolved fragments.

Goal

- Find and explain the dependence of ozone bleaching on prior treatments, including oxygen delignification and different pulping processes

Approach



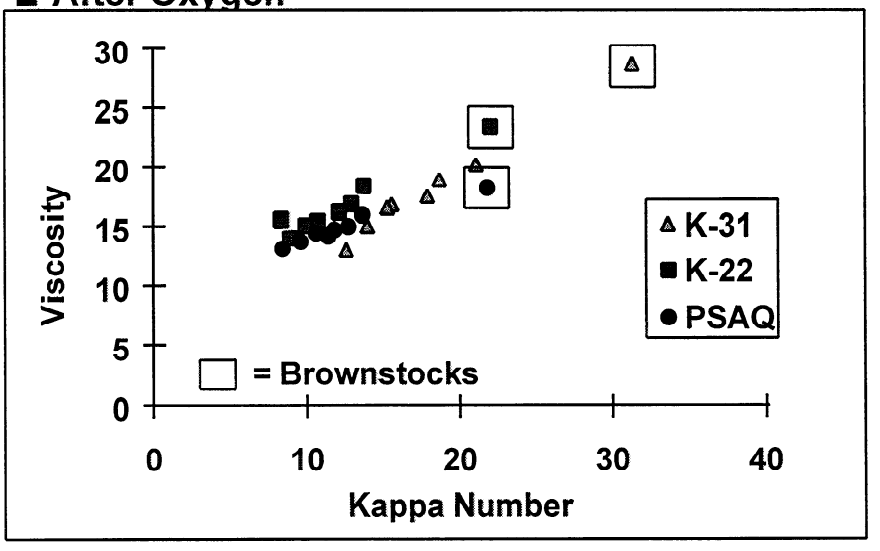
•Approach

■ Analyses

- ◆ Pulp
  - ✦ kappa number
  - ✦ klason & acid sol. lignin
  - ✦ viscosity (NaBH4)
  - ✦ cellulose MWD
  - ✦ functional groups
  - ✦ strength
  - ✦ brightness
  - ✦ yield
- ◆ Filtrates
  - ✦ TOC
  - ✦ dissolved sugars
  - ✦ MWD
  - ✦ elemental analyses
  - ✦ acidity
  - ✦ lignin

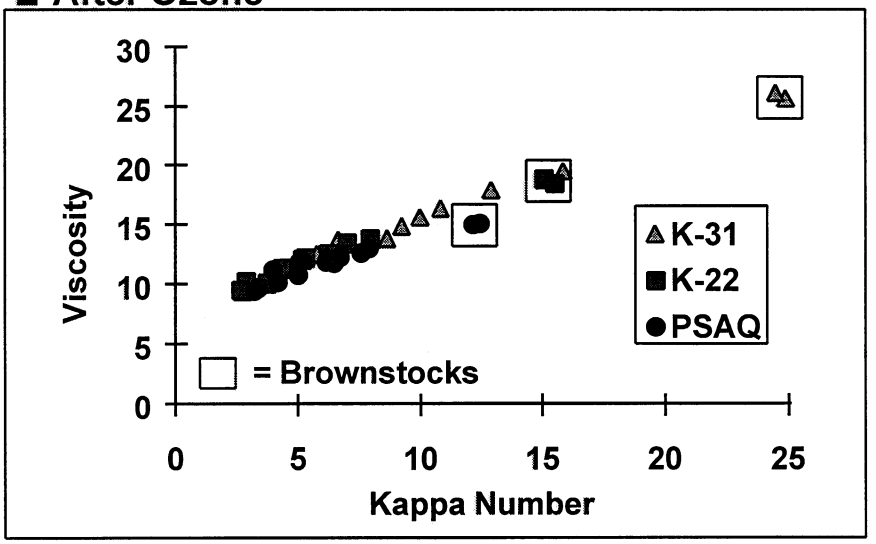
Results

■ After Oxygen



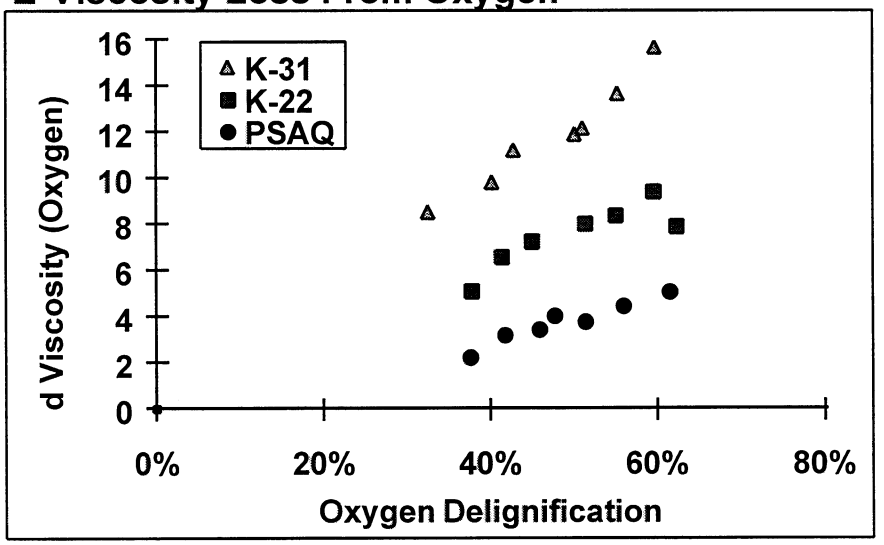
Results

■ After Ozone



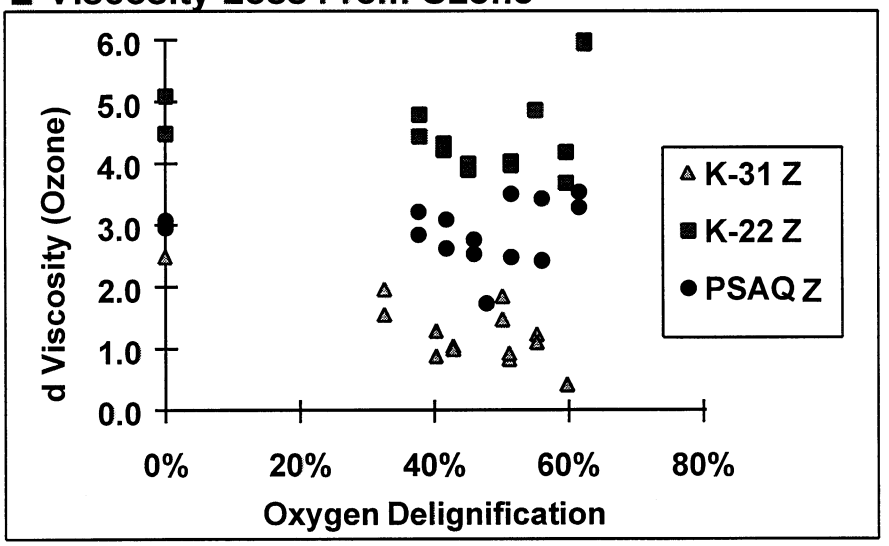
Results

■ Viscosity Loss From Oxygen



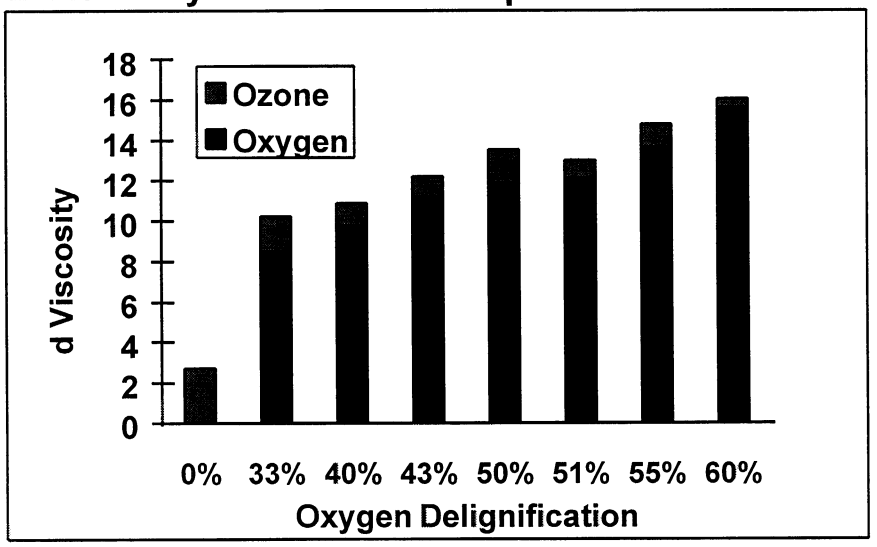
Results

■ Viscosity Loss From Ozone



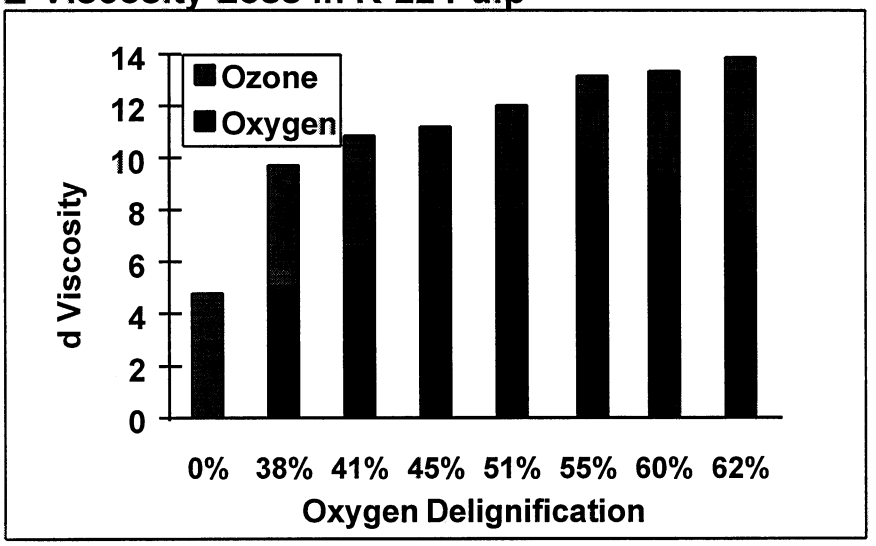
Results

■ Viscosity Loss in K-31 Pulp



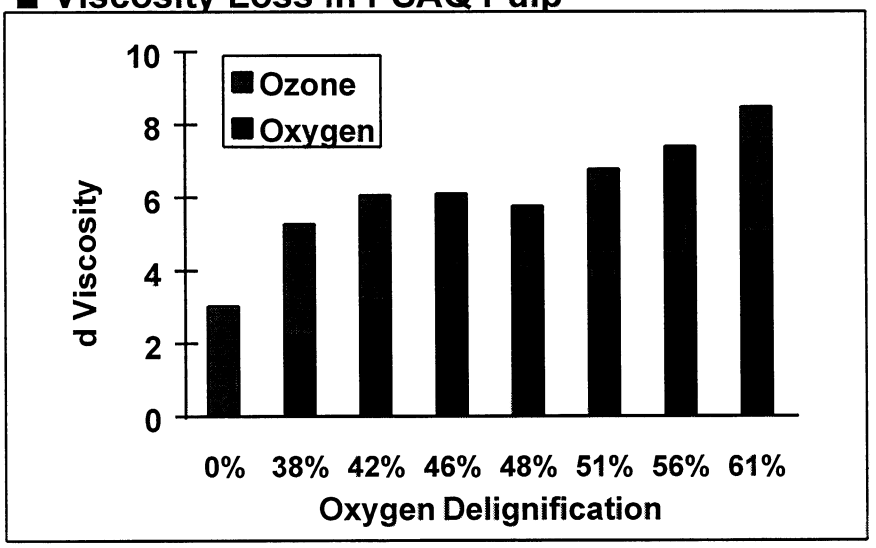
Results

■ Viscosity Loss in K-22 Pulp



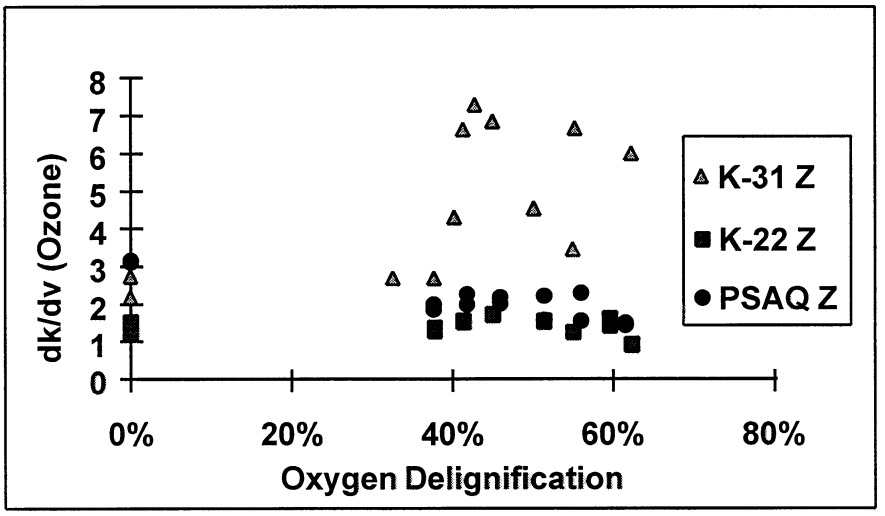
Results

■ Viscosity Loss in PSAQ Pulp



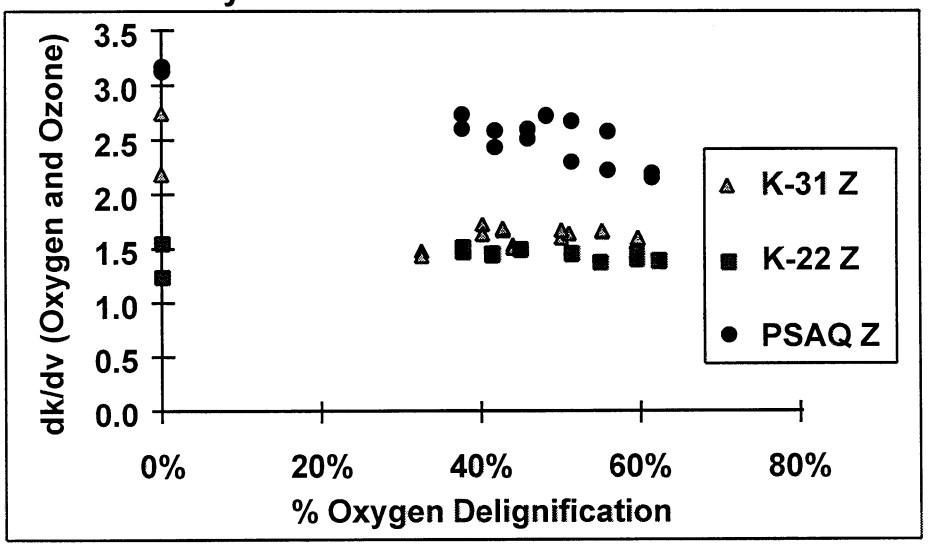
Results

■ Selectivity of Ozone



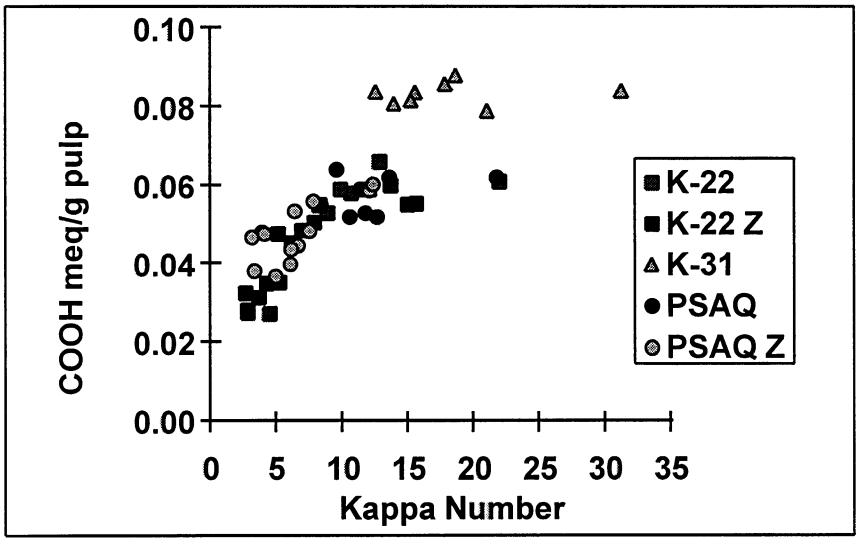
Results

■ Selectivity Overall



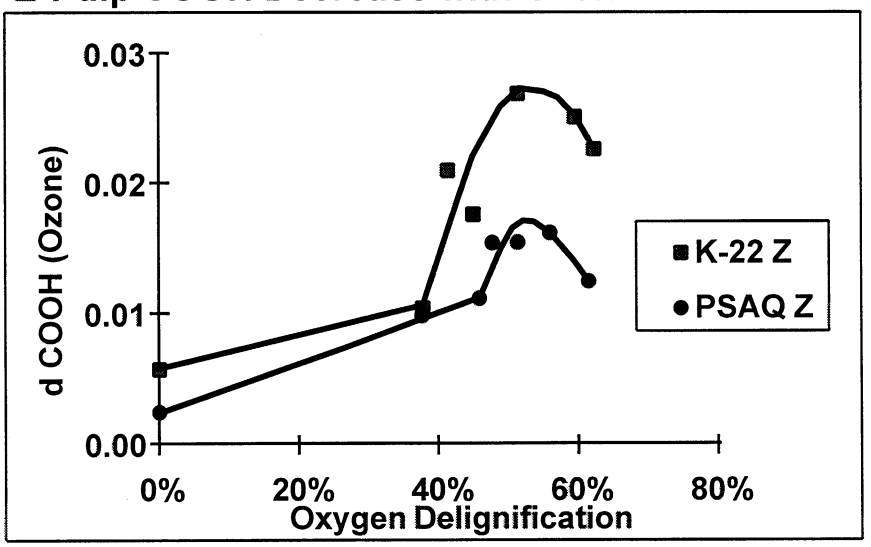
Results

■ COOH on Pulp



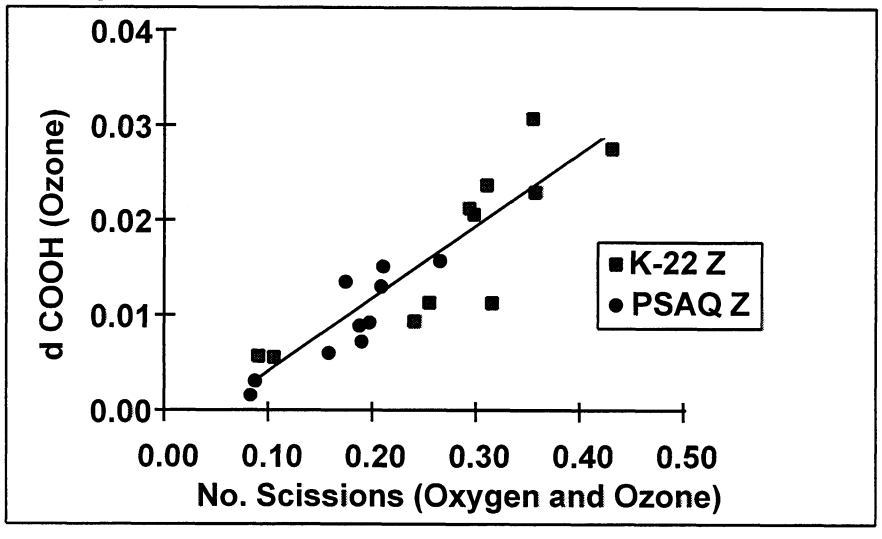
Results

■ Pulp COOH Decrease with Ozone



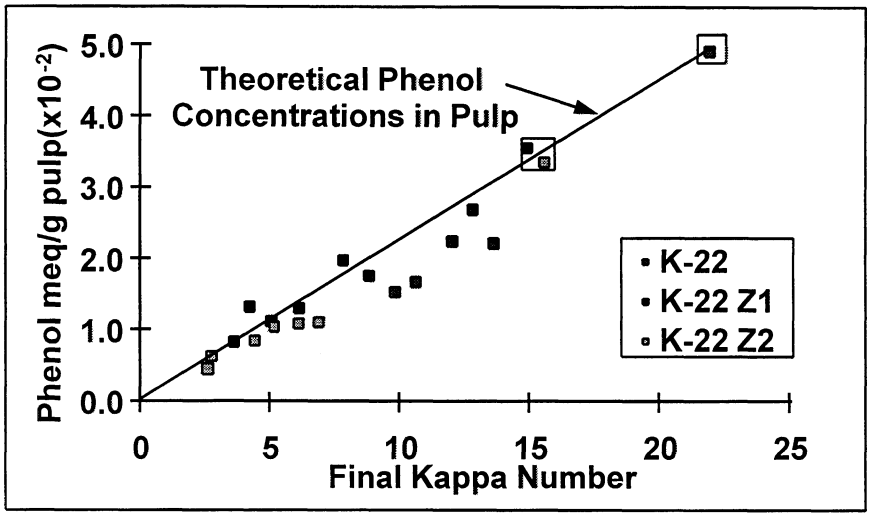
Results

- Pulp COOH Decrease vs. Number of Scissions



Results

- Phenol Concentrations



Summary

- Pulping conditions strongly affect oxygen and ozone selectivity
- Oxygen delignification causes changes in ozone selectivity
- Ozone selectivity of oxygen delignified pulps peaks between 40 and 50 % oxygen delignification
  - lignin removal improved for high lignin pulps
  - viscosity loss inhibited for all pulps

Summary

- Carboxylic acid content on ozonated pulp decreases with oxygen delignification
- Carboxylic acid decrease may be related to loss of small, acidic fragments of carbohydrates
- Oxygen pretreatment depolymerizes carbohydrates and lignin and allows ozone to introduce more solubilizing carboxylic acid groups
- Oxygen selectively removes phenols in lignin, but subsequent ozone treatment produces lignin more similar to the parent structure

Future Activity

- Complete the described experiments
- Extend oxygen-ozone studies to more advanced measures of paper properties (in concert with Pulping and Bleaching)
- Fully bleach selected sequences and reevaluate conclusions regarding optimal bleaching interactions
- Begin mechanistic studies to investigate the chemistry of oxygen and ozone with lignin and carbohydrates on a molecular level

Acknowledgments

- Lenong Allison
- Elizabeth Althen
- Pulping and Bleaching Group
- Chemical Analysis Group
  - Ersdel Estridge
  - Kathleen Poll

Fundamentals of Bleaching Chemistry
F015

High Efficiency Peroxide Bleaching

Bio-Assisted Bleaching

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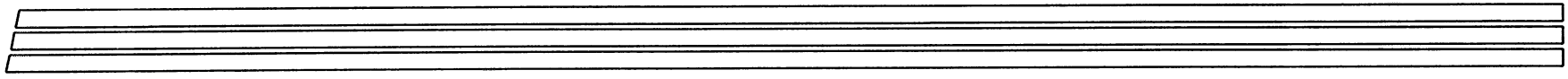


F015: High Efficiency Peroxide Bleaching - Introduction

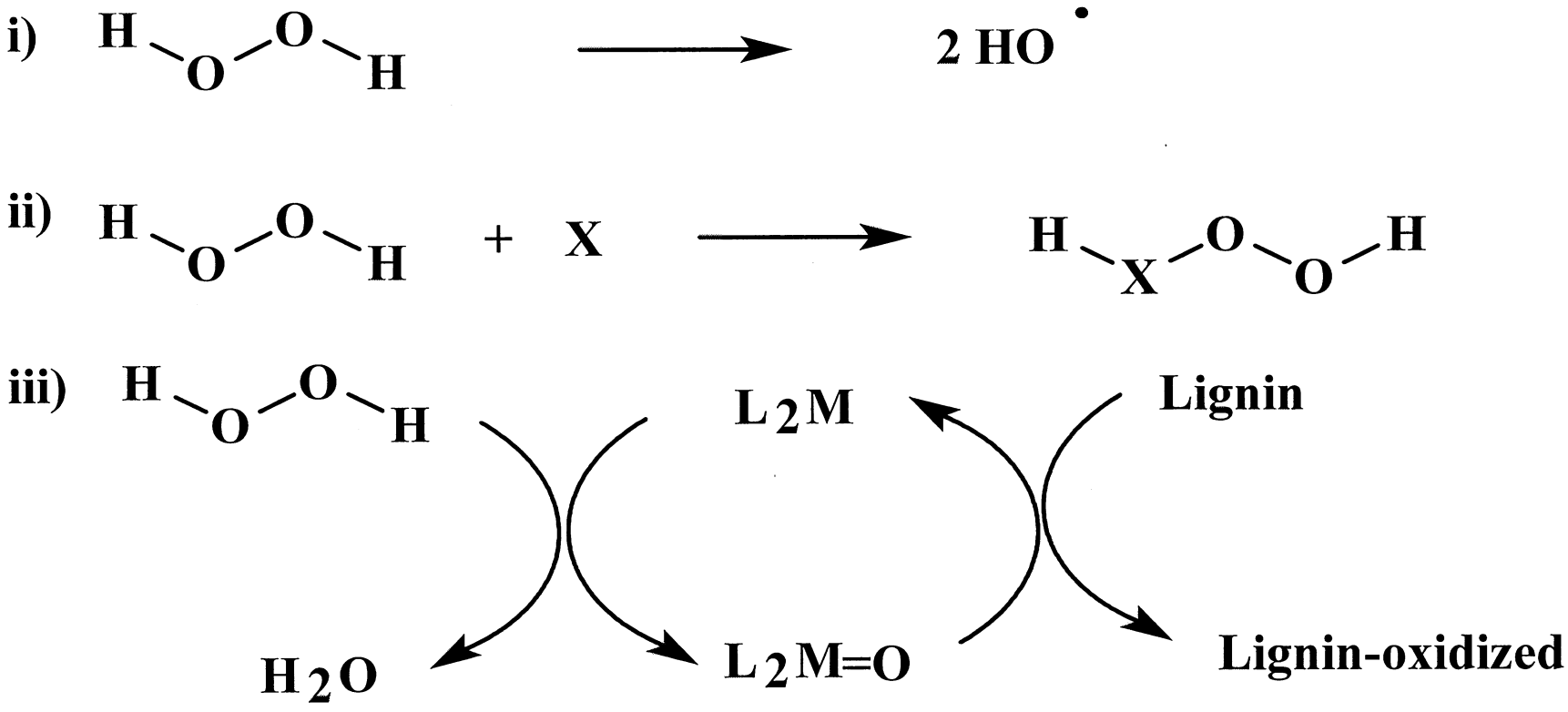
- Research Goals
  - Explore use of activators/catalyst for H_2O_2
  - Determine fundamental chemistry of peroxide delignification

- Industrial Application

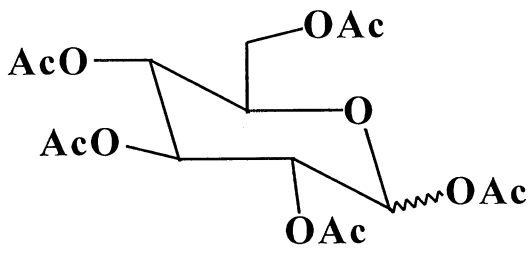
  Develop low capital bleaching technologies to improve ECF & TCF operations.

F015 - Peroxide Activation: Introduction

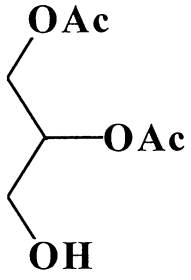
- Activation Chemistry

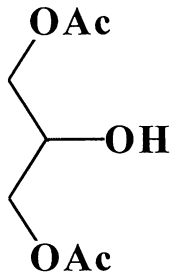


F015 *Peroxide activation:activators/FY 95-96*

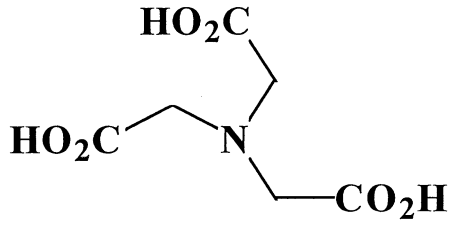


Pentacetyl Glucose

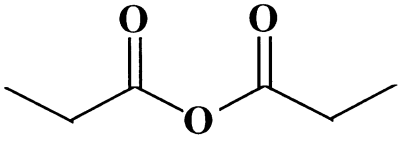




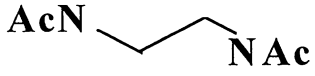
Diacetin



Nitriloacetic Acid



Diethyl Pyrocarbonate



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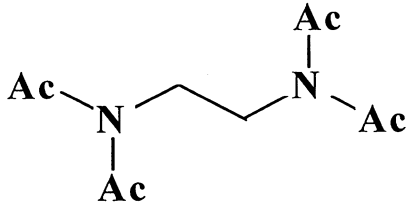

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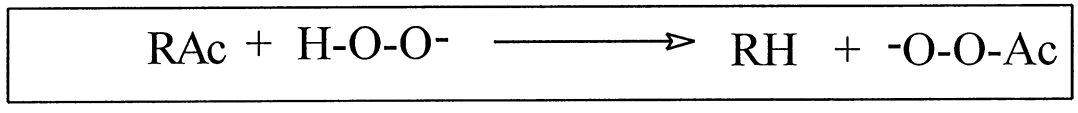
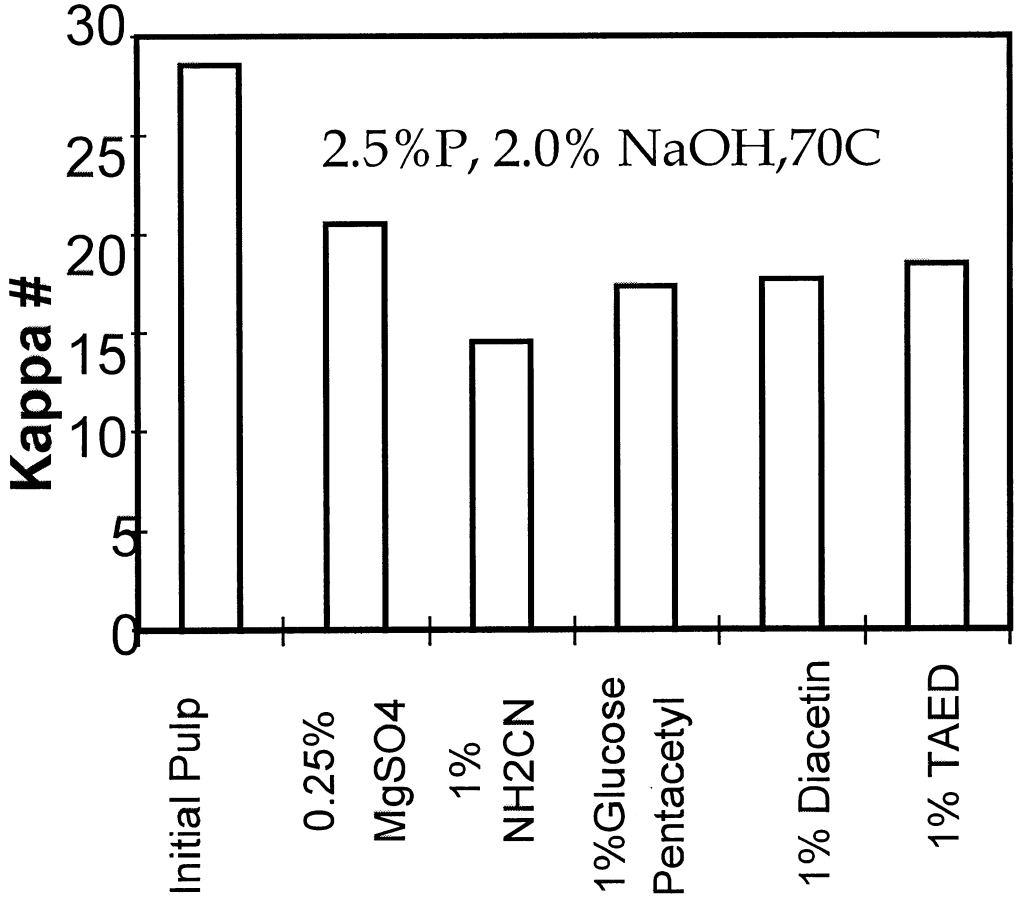
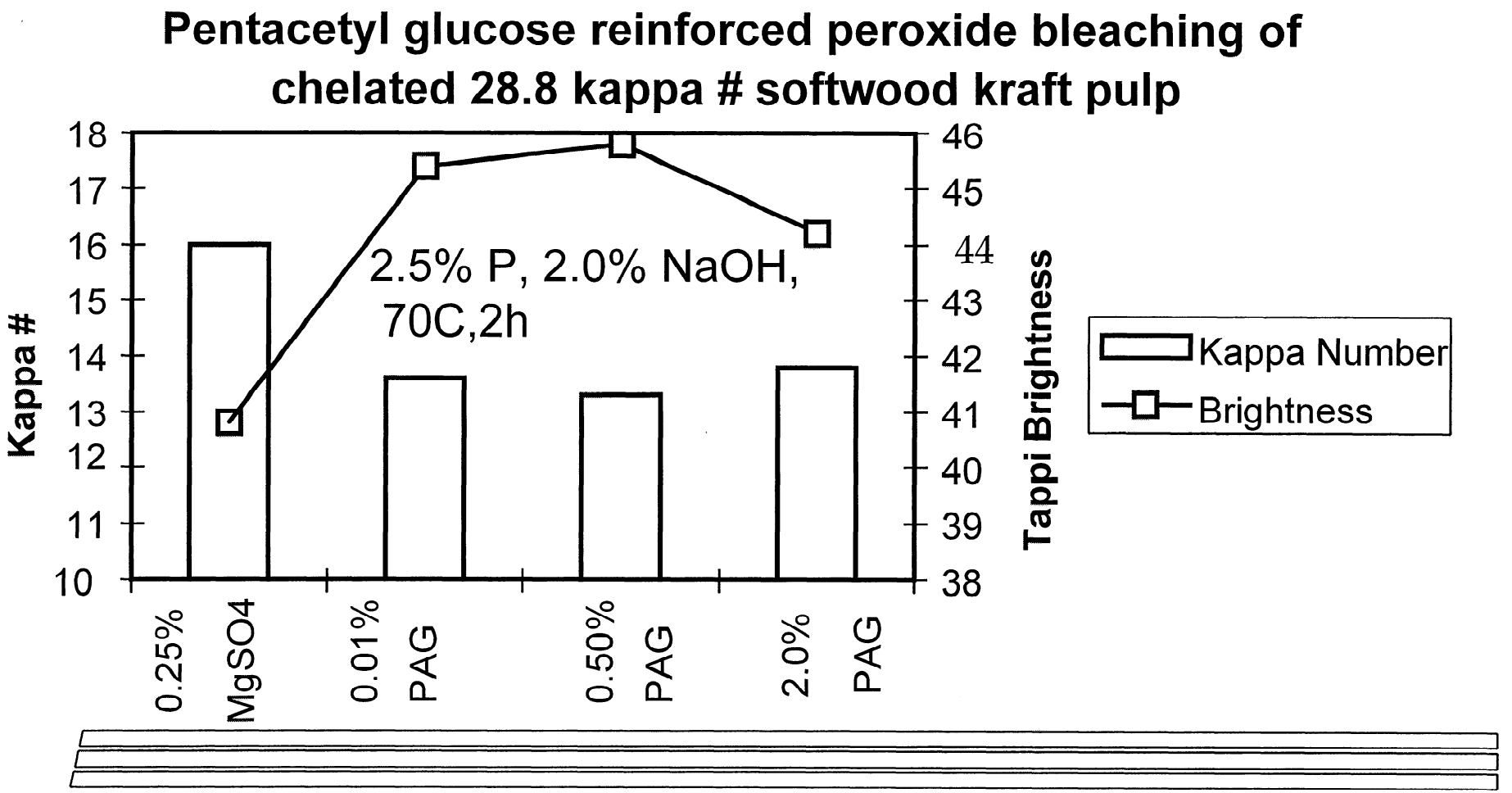


F015 *Peroxide activation:activators/FY 95-96*

- NH_2CN optimal benefit
- Additives differ in MW & stoich. chemistry



F015 - Peroxide Activation



F015 - *Summary of Stoichiometric peroxide activation*

Benefits

- Pentacetyl glucose, Diacetin and TAED enhance alkaline P
  -delignification by 10%
  -Tappi bright. by 15%
  -peroxide consumption reduced by 20%
- Diethyl pyrocarbonate aid acidic P

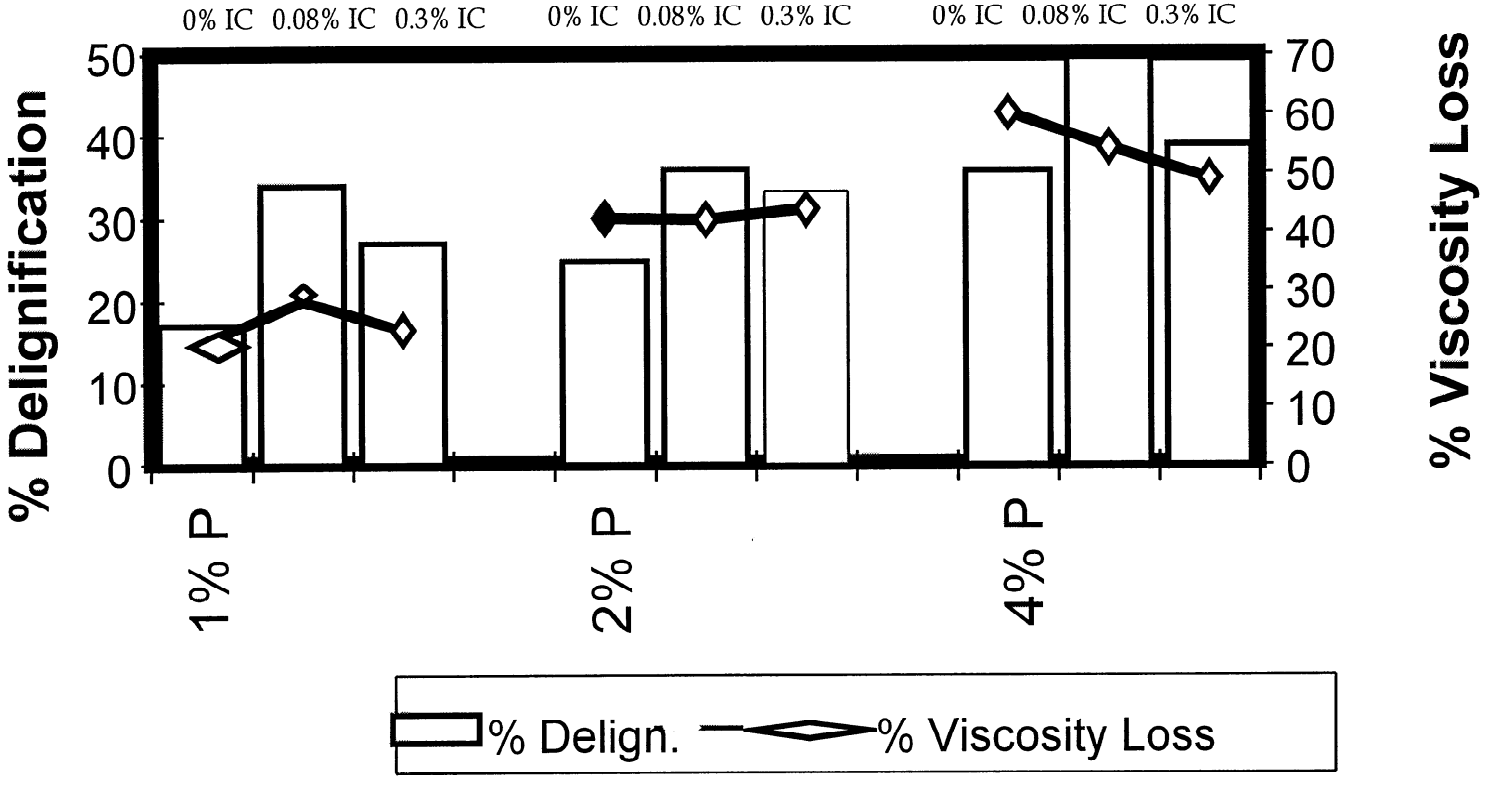
Difficulties

- Stoichiometric activation
- Peroxide activation ceiling

F015 - *Catalytic Peroxide Activation*

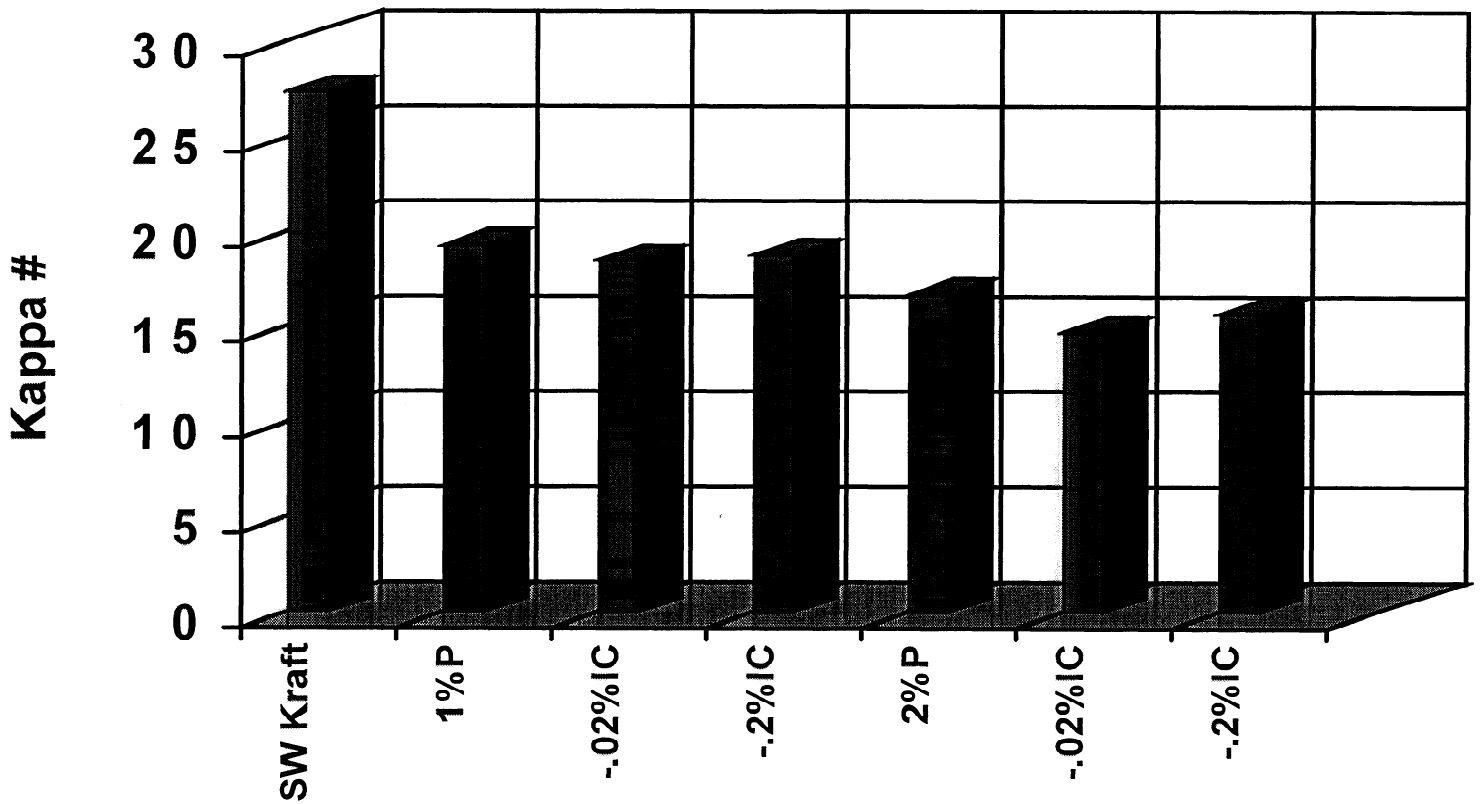
- Research Need
  - catalytic technology to enhance oxidative power of H_2O_2
    - » $Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^o=1.358$ v
    - » $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^o=1.776$ v
    - » $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ $E^o=2.076$ v
- Several industrial catalyst (IC) available

F015 - Catalytic Peroxide Activation: Use of industrial catalyst to improve alkaline peroxide bleaching of O-delign SW kraft.

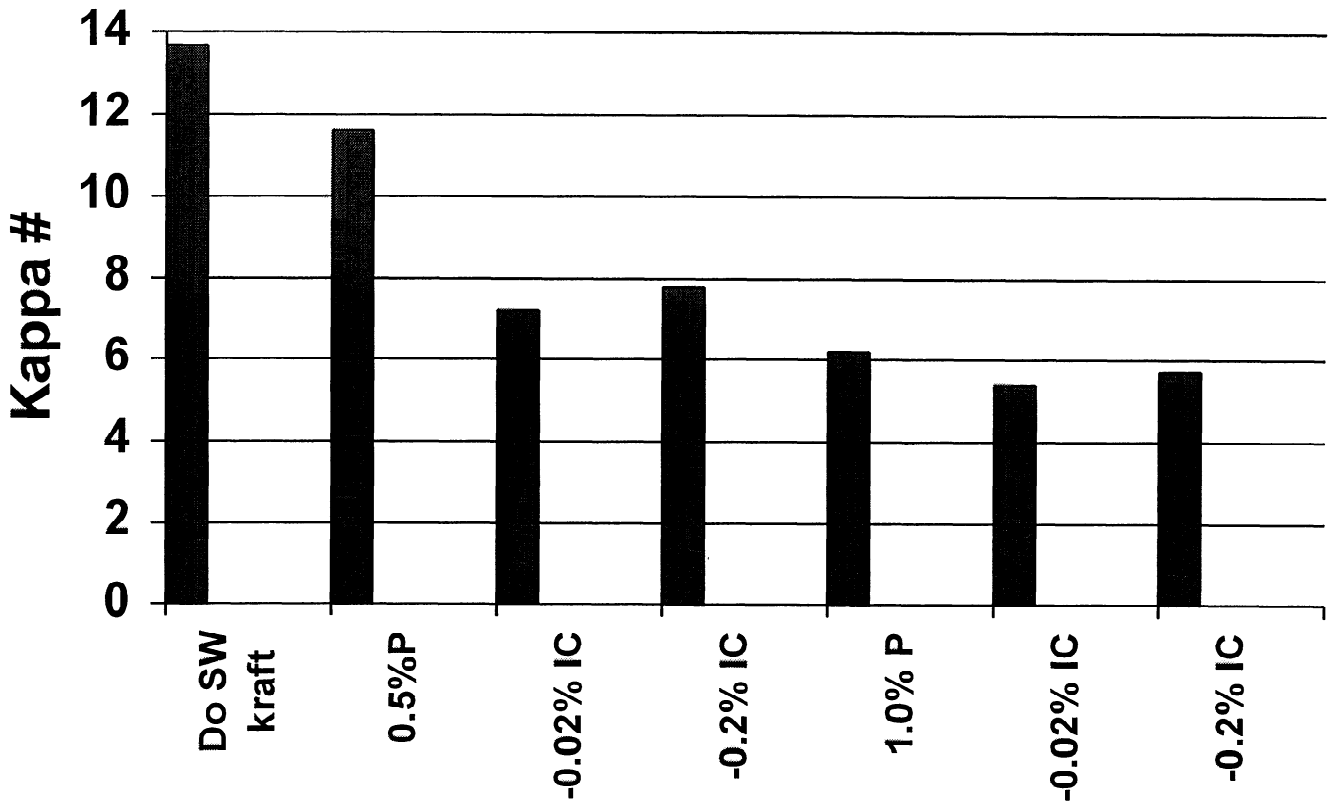


O-Delign. Softwood Kraft (16.6 K#), P-stage 70°C, 4 h

F015 - Catalytic Peroxide Activation: Use of industrial catalyst to improve alkaline peroxide bleaching of SW kraft.



F015 - Catalytic Peroxide Activation: Use of industrial catalyst to improve alkaline peroxide bleaching of Do SW kraft.



F015 - Catalytic Peroxide Activation: Application of industrial catalyst to improve alkaline peroxide bleaching.

Summary

Catalyst provides optimal benefits with low charges

Delignification benefits: SW kraft: 8%, O: 15%, D: 20%

Catalyst sensitive to temperature & bleaching conditions

F015 - Catalytic Peroxide Activation Summary & Research Needs

- Demonstrated potential for P-stage catalyst
- Need to optimize and pursue commercial applications of current catalyst technology
- Future P-delignification technology requires a improved understanding of the fundamentals of P bleaching

F015 -Fundamentals of Peroxide Bleaching - Introduction

- Research Goal
  - Determine fundamental chemical reactions involved in peroxide delignification
    - » including P, P* , & P-act

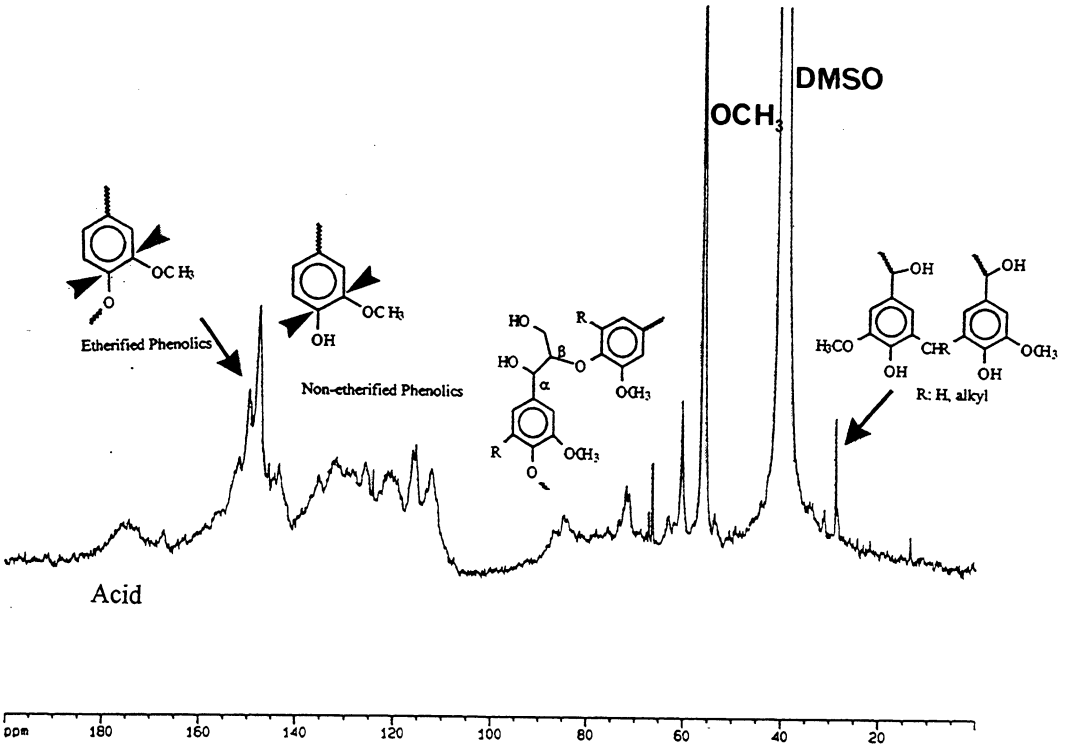
F015 -Fundamentals of Peroxide Bleaching - Introduction

- General Approach:

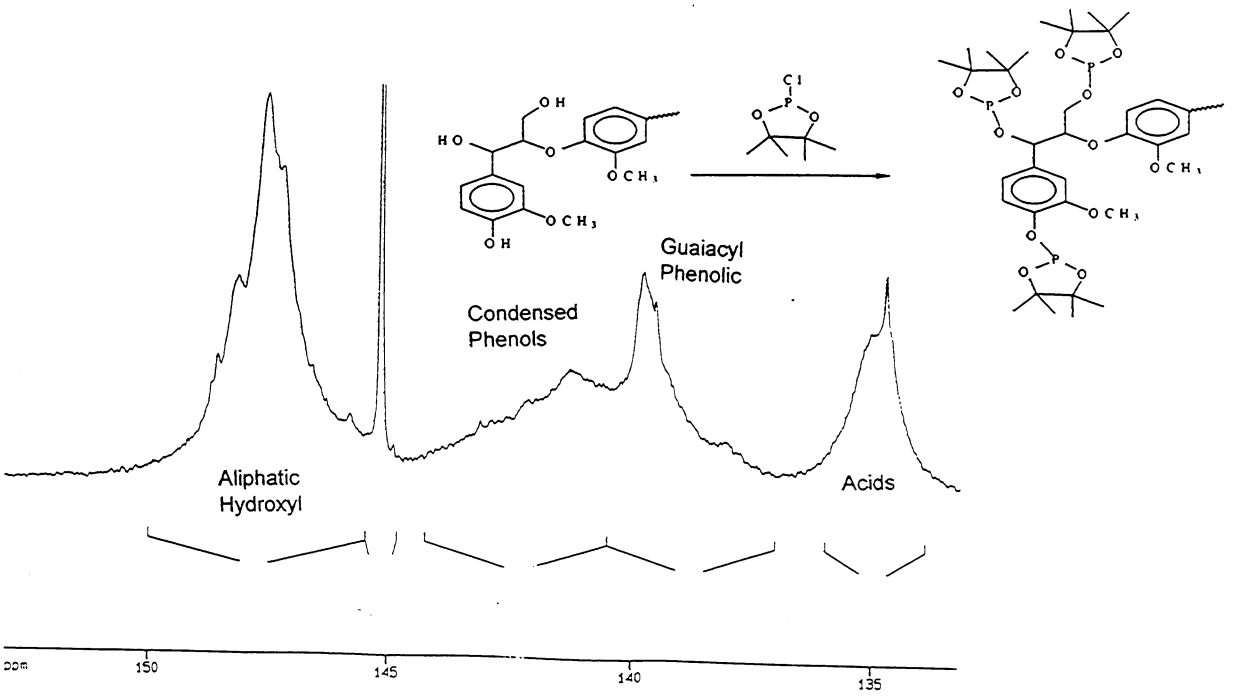
	Kappa #1
– chelated SW kraft pulp	28.4
» 2.5% P/70°C/4h	17.0
» 2.5% P/90°C/4h	16.9
» 1.25% P/110°C/1h	13.6
» 2.5% P/110°C/1h	10.3
» 2.5% P/70°C/4h//0.5% NH_2CN	14.0
» 7.5% P/70°C/4h//1.5% NH_2CN	8.1

- Isolate & characterize residual lignin
- Decipher reaction mechanisms

^{13}C NMR analysis of residual lignin isolated from softwood kraft pulp bleached with 2.5% H_2O_2 at 70°C for 4 h.



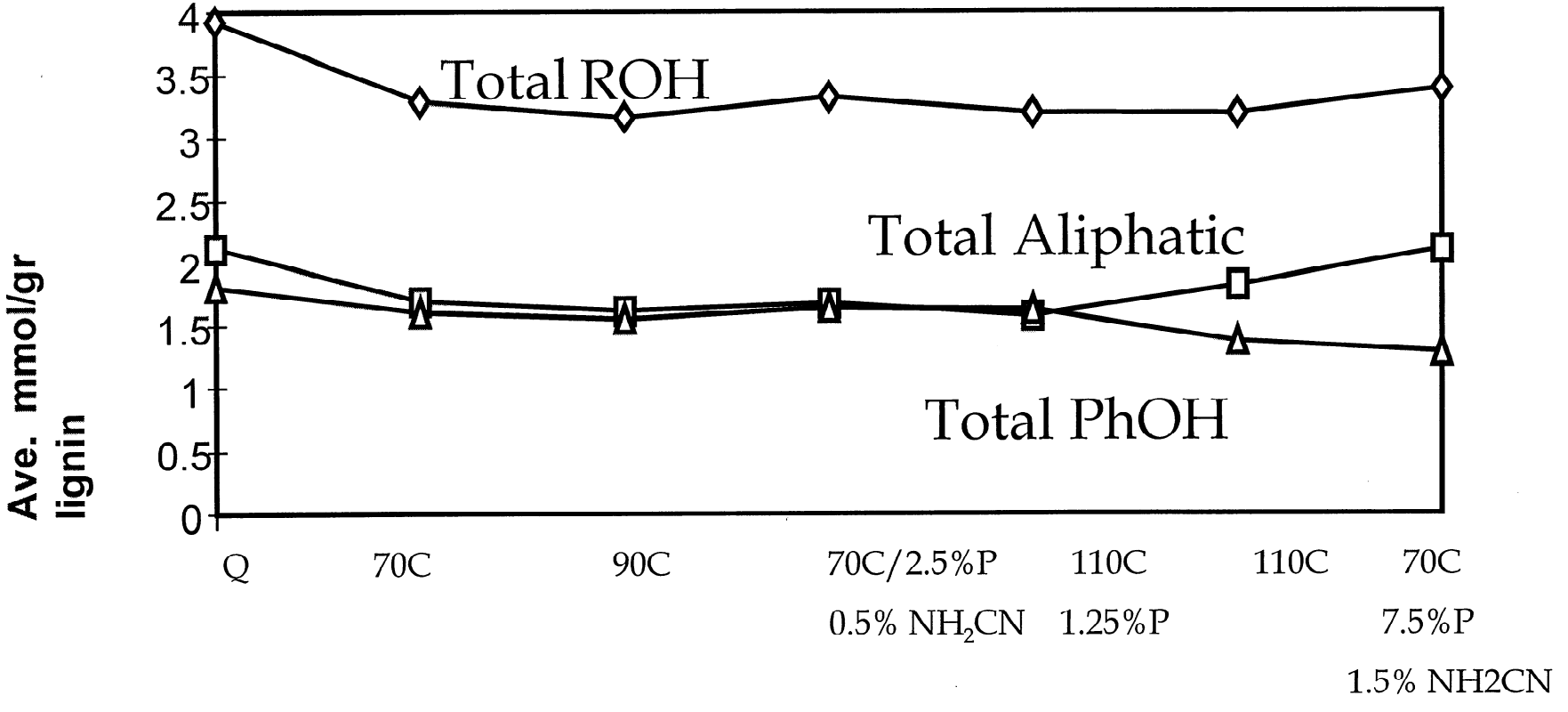
Oxyphosphitylation and ^{31}P NMR analysis of residual lignin isolated from softwood kraft pulp bleached with 2.5% H_2O_2 at 70°C for 4 h.



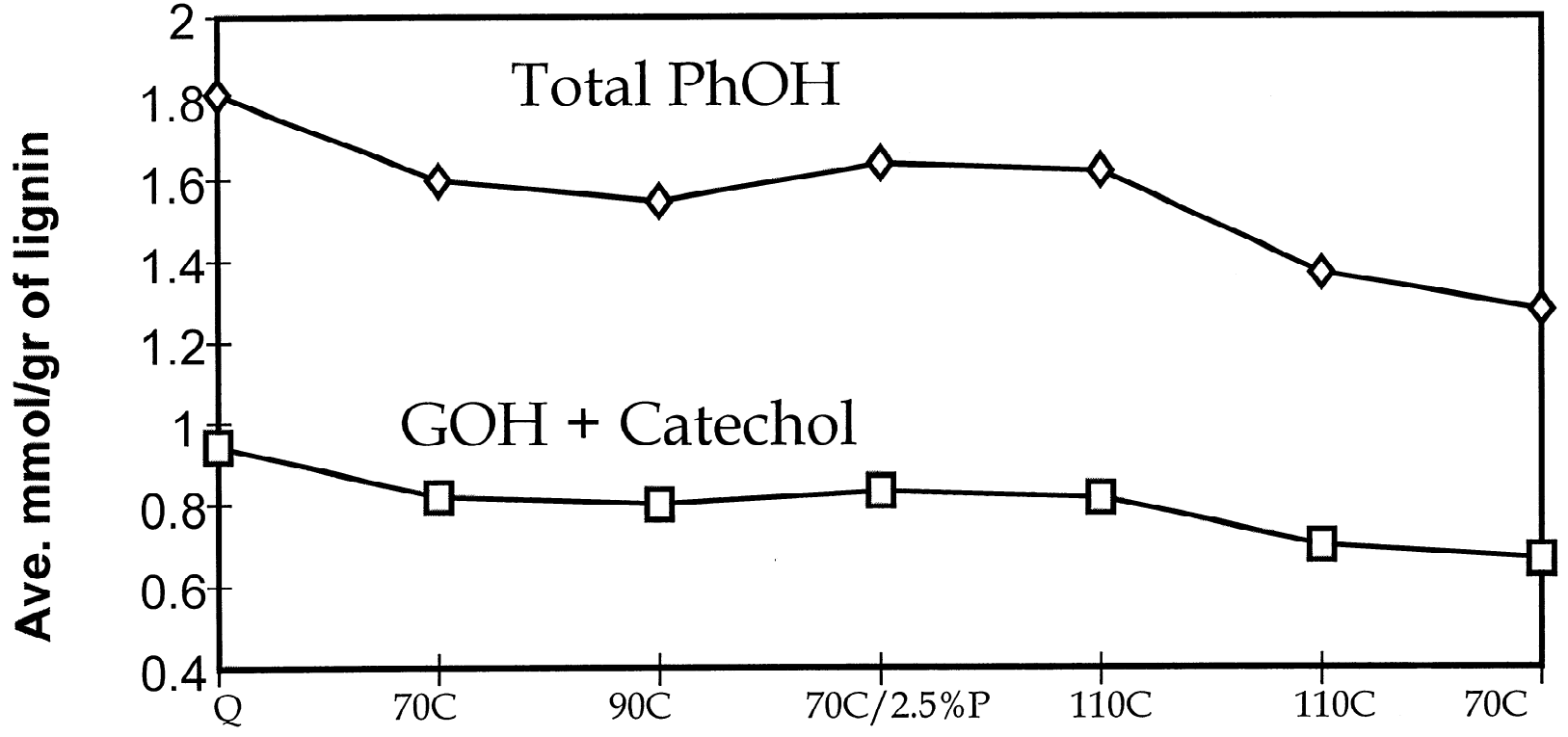
F015 -Residual Lignin Analysis: ^{13}C-NMR
Functional Group Analysis/Relative Amounts

Residual Lignin	Acid	Total Non-Phenolic & Phenolic (ratio)	Cα, Cβ Linkages	Condensed Diarylmethane
Initial	0.3	2.1 (1.0:1.8)	1.1	0.1
2.5%P 70°C	0.4	2.0 (1.0:1.6)	1.1	0.1
2.5% 90°C	0.4	2.1 (1.0:1.6)	1.0	0.1
2.5%P 110°C	0.7	2.1 (1.0:1.3)	1.1	0.1

F015 -Residual Lignin Analysis
^{31}P-NMR

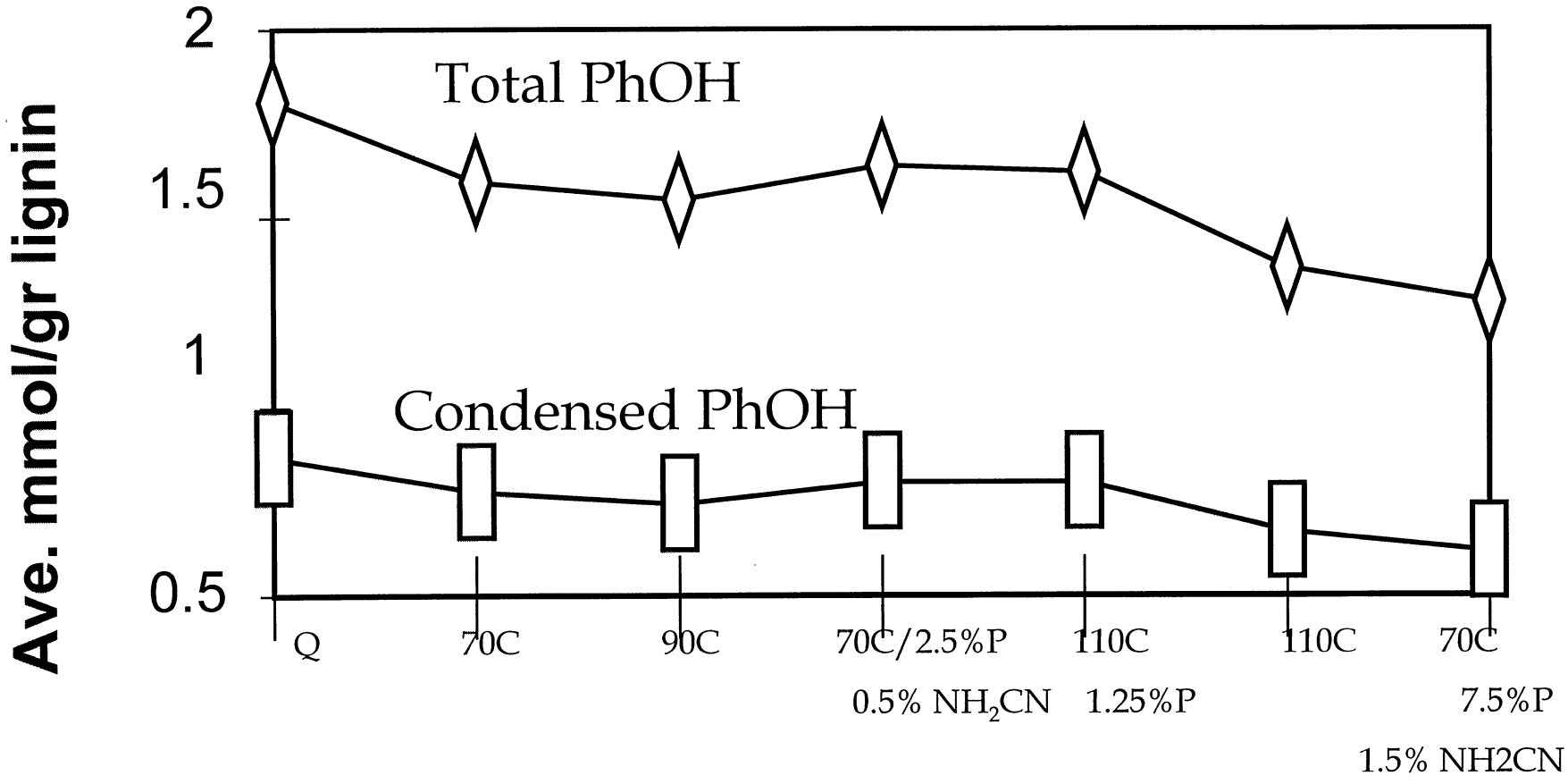


F015 -Residual Lignin Analysis
^{31}P-NMR

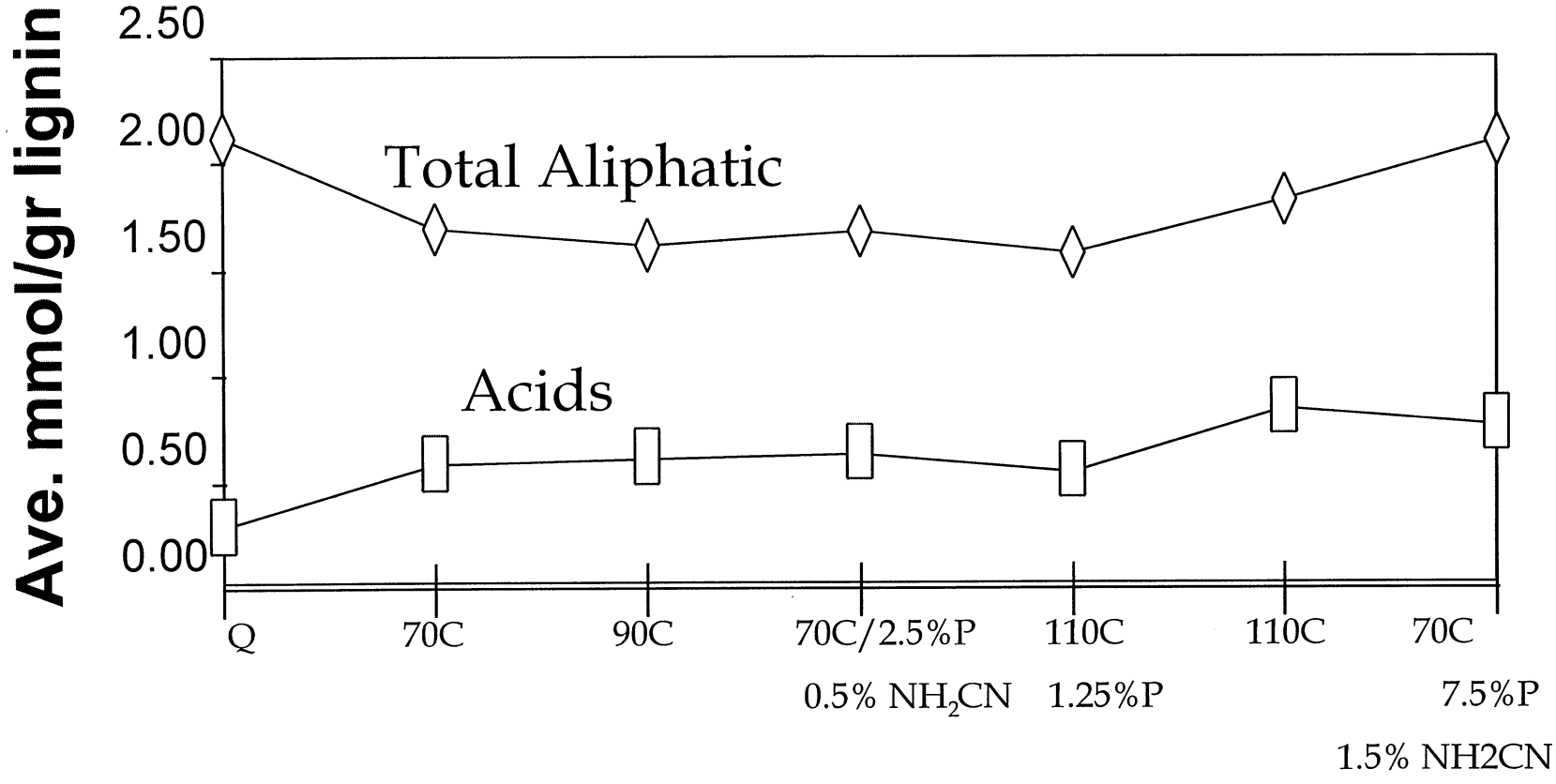


F015 -Residual Lignin Analysis

^{31}P-NMR



F015 -Residual Lignin Analysis
^{31}P-NMR



F015 -Fundamentals of Peroxide Bleaching - Conclusions

- Condensed diaryl-structures resistant to bleaching
- Peroxide conditions that remove ca. <45% of lignin appear to have comparable residual lignin.
- P delignification removing more than 45% significantly begin to alter residual lignin structure

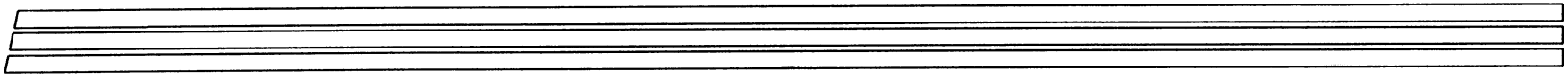
- Residual lignin is enriched in non-conjugated ketones (FT-IR) >>>deactivating group

F015 -Fundamentals of Peroxide Bleaching - Conclusions & Future Directions

- Portion of kraft lignin is reactive to H_2O_2.
- Nature of residual lignin significantly influence P.
- May be possible to alter reactivity via pretreatments.

F015: *Fundamentals of Bleaching Chemistry*

Bio-Assisted Bleaching



F015: Bio-assisted Bleaching - Introduction

Hemicellulase Pretreatments

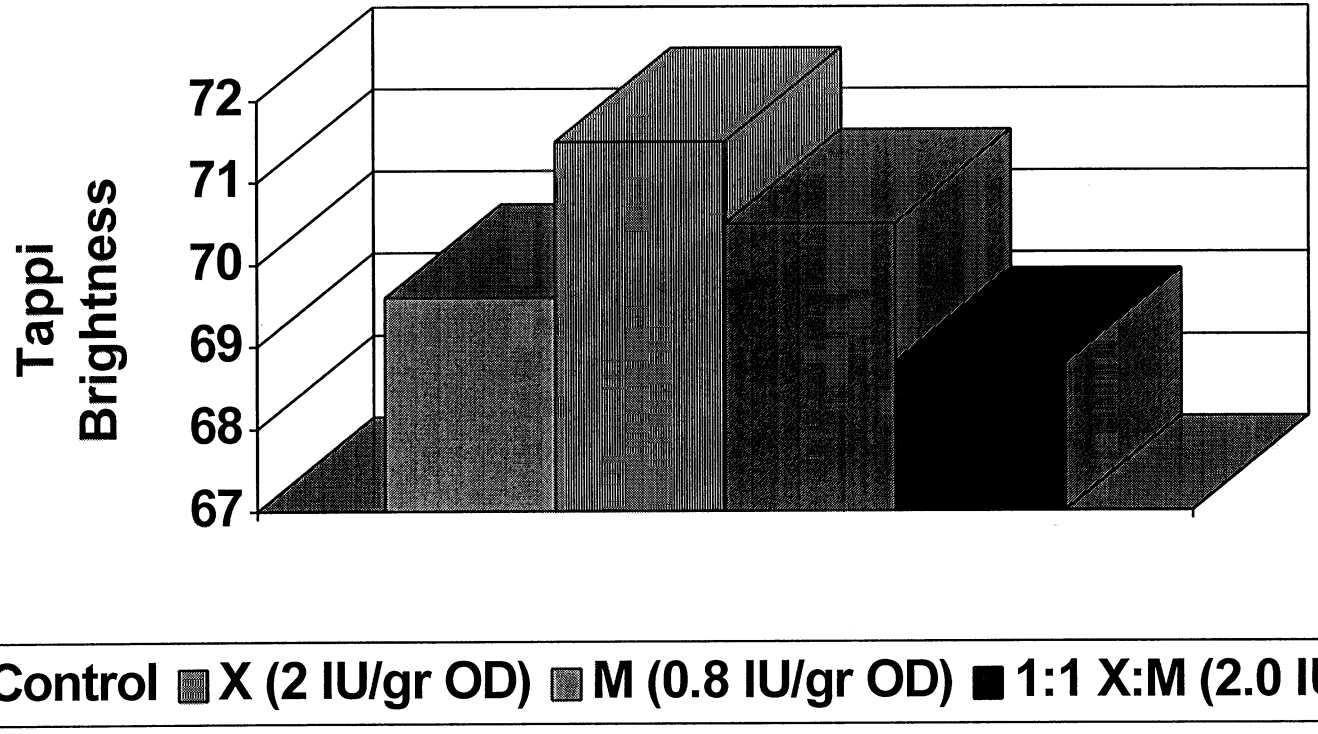
F015: Bio-assisted Bleaching - Introduction

- FY 95-96 Research Goals
  - –Examine use of xylanase/mannanase to improve biopretreatment.

- Industrial Application
  - – Improve current ECF operations

F015: Bio-assisted Bleaching - Xylanase/Mannanase Results

Brightness values for softwood kraft pulp pretreated and DEDE bleached

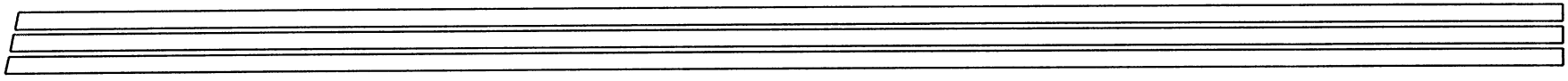


F015: Bio-assisted Bleaching - Xylanase/Mannanase Results

- No benefits observed for softwood kraft pulps employing M for either DEDE or DEopD bleaching sequences.
- Xylanase effluents appear to contain hexenuronic acids
  - unsaturated hemis shown to react with Z & D

F015: Bio-assisted Bleaching - Introduction

Exploration of Laccase Mediator Systems for Delignifying Kraft Pulps



F015: Bio-assisted Bleaching - Introduction

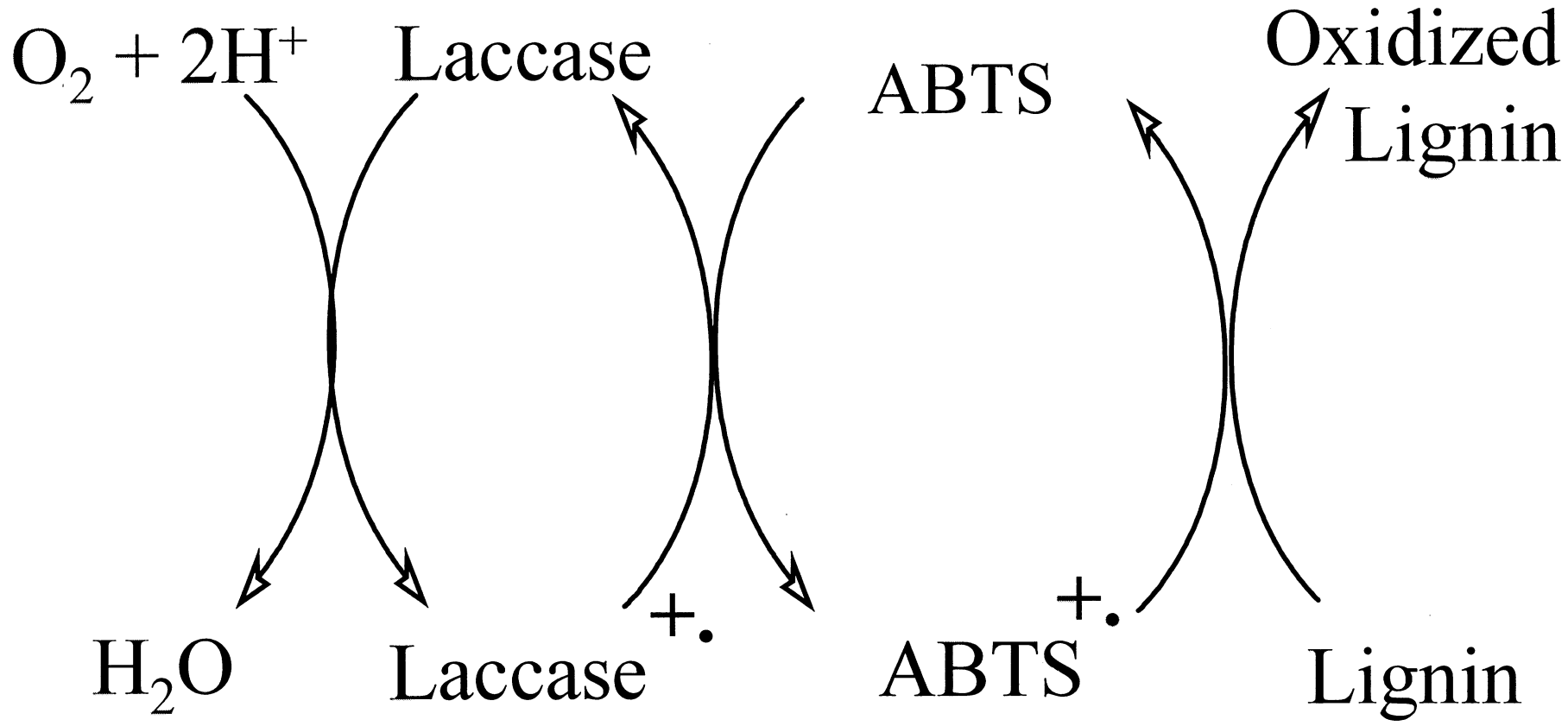
- FY 95-96 Research Goals
  - develop laccase/mediator system
  - explore bleaching chemistry

- Industrial Application

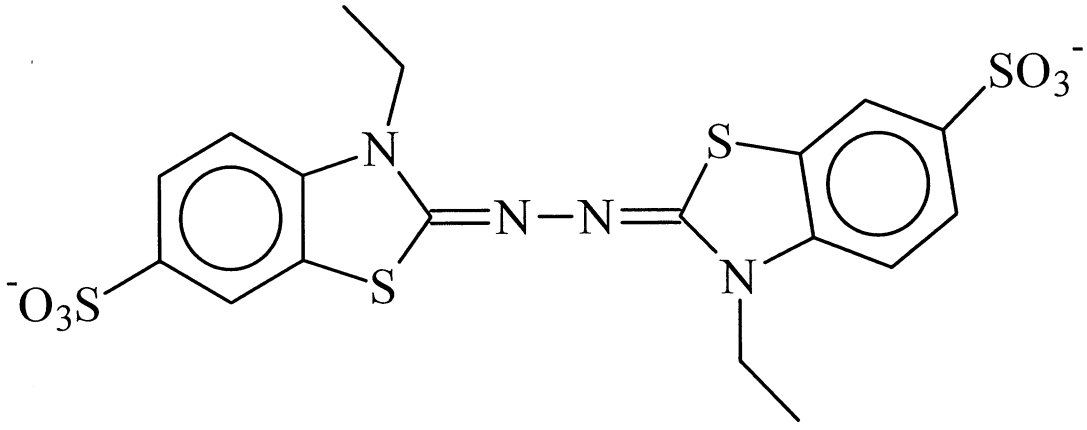
  Develop new bleaching technologies improved pulp properties.

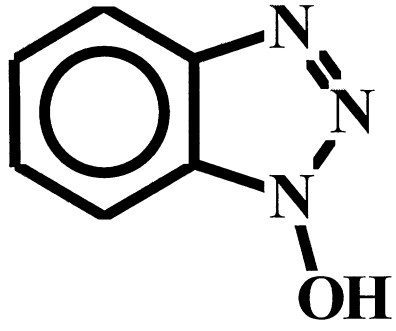
F015: *Bio-assisted Bleaching - Introduction*

Laccase Mediator System (LMS) - Delignification



F015: Bio-assisted Bleaching - Introduction

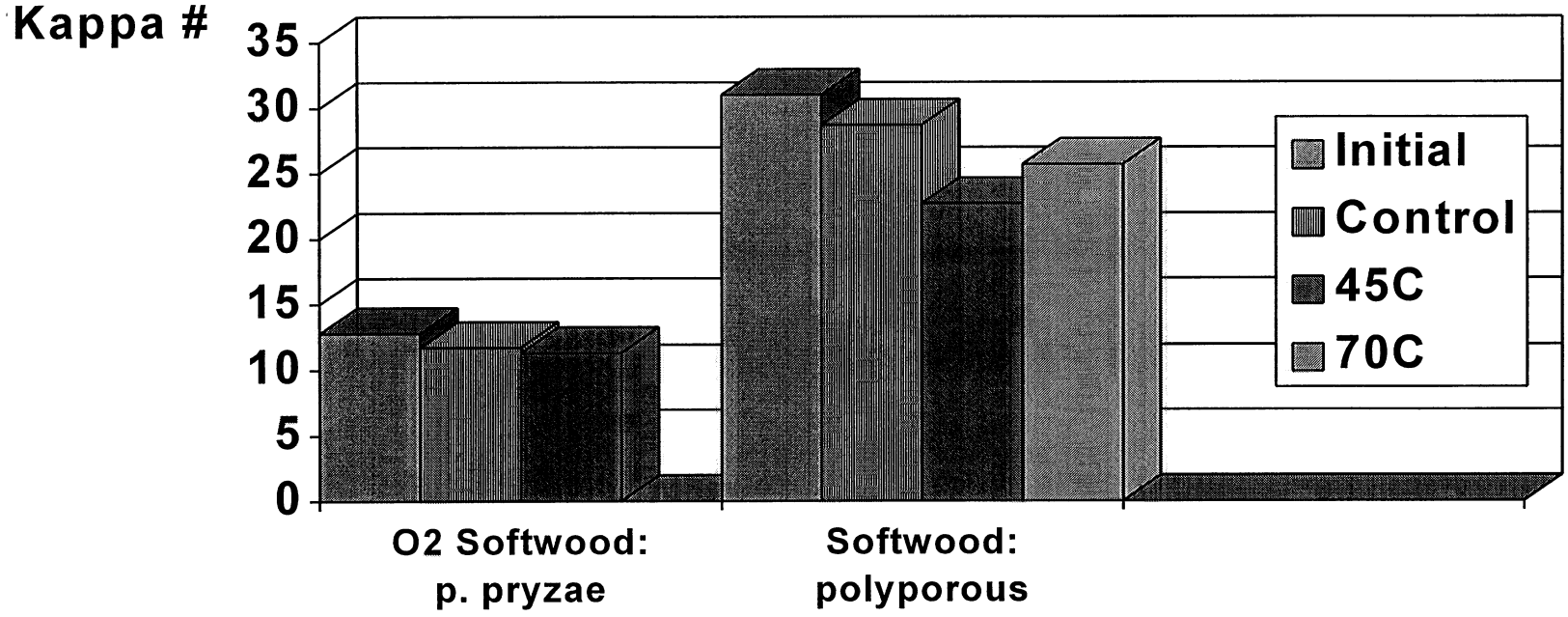




ABTS	NHB
1st Generation	2nd Generation

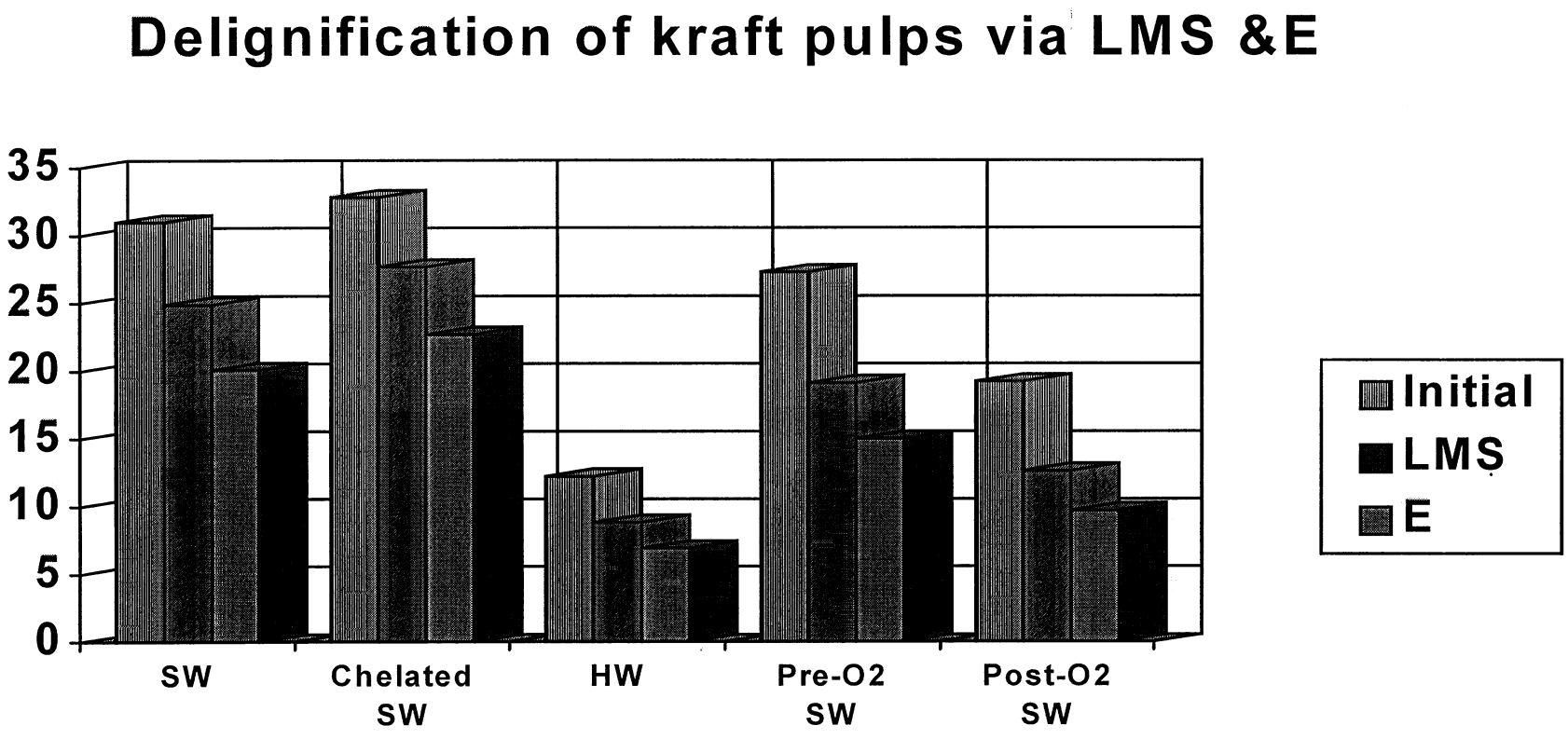
F015: Bio-assisted Bleaching - Results

SW kraft after LMS & E-stage



Exp. Conditions: 24 h, pH:4.0, no O_2 pressure

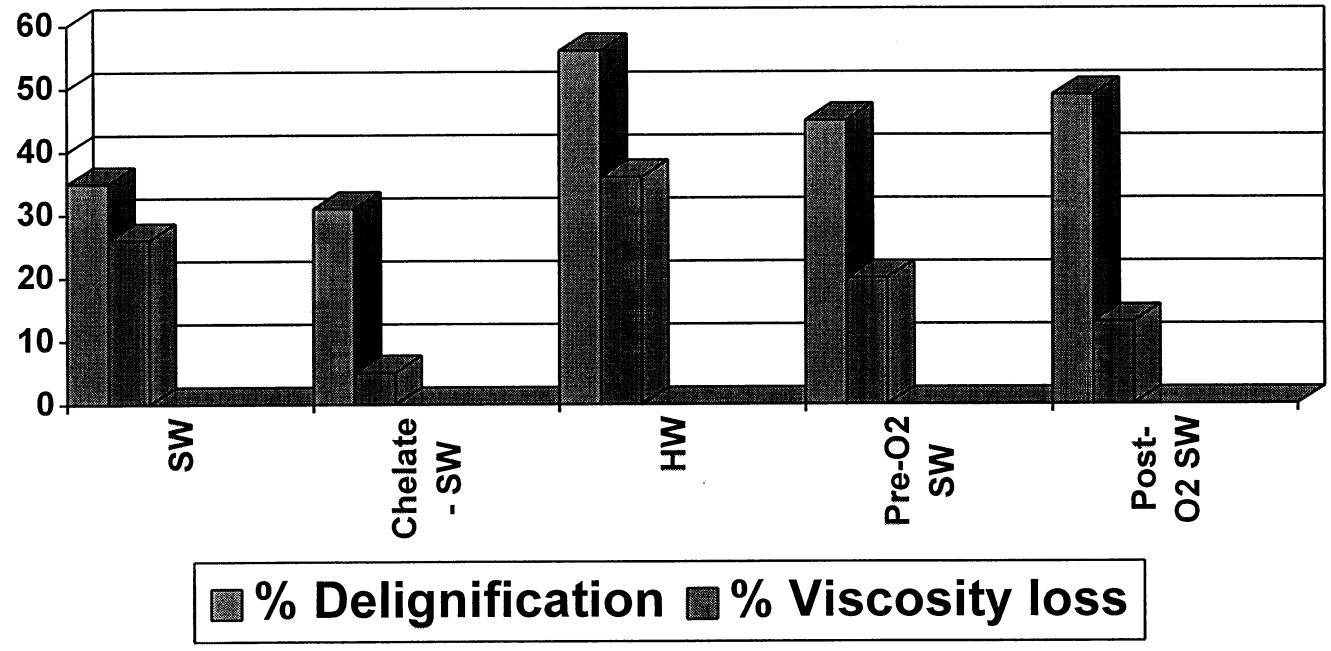
F015: Bio-assisted Bleaching - Results



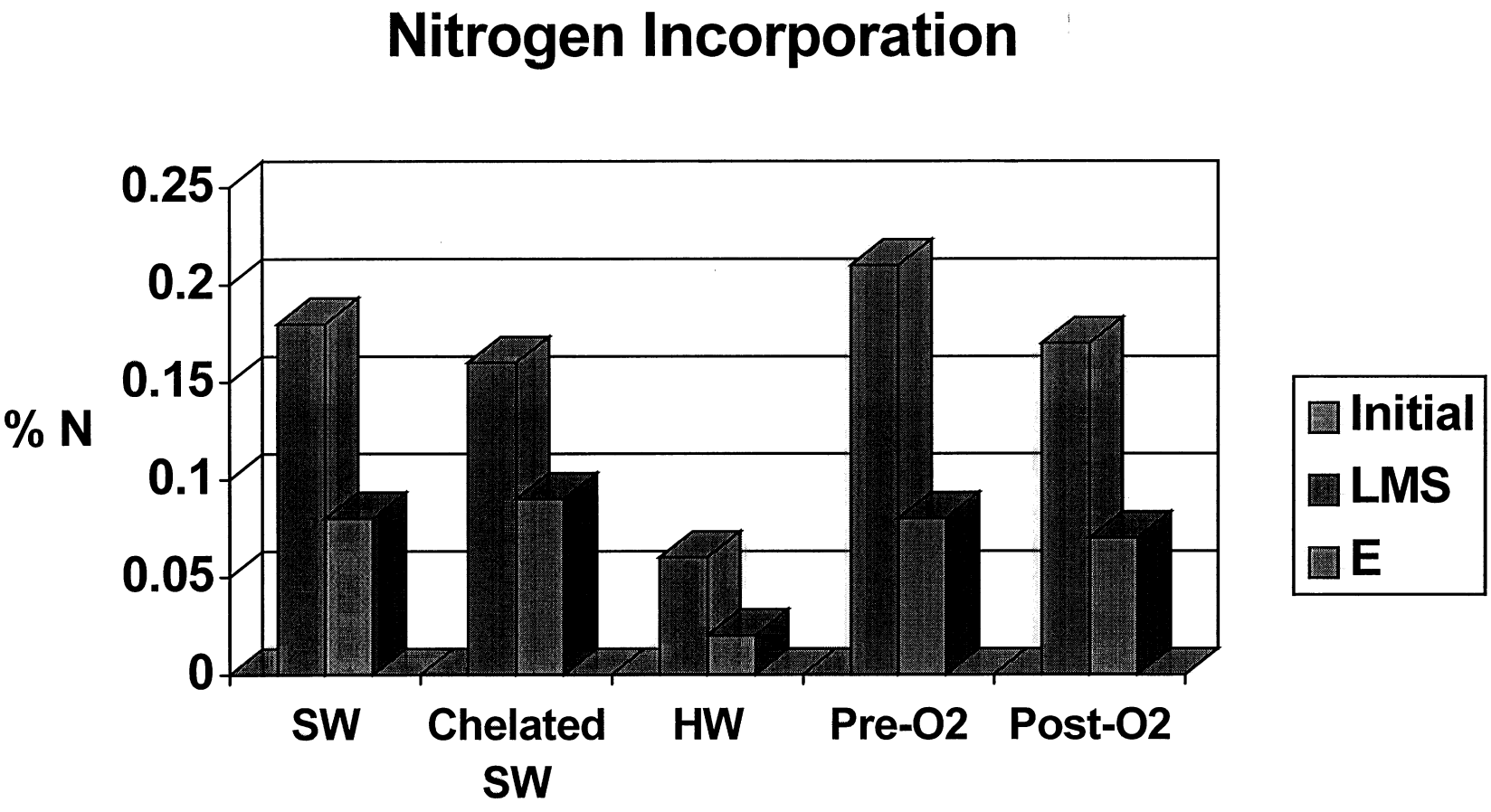
Exp. Conditions: 10 barr O_2, pH: 4

F015: *Bio-assisted Bleaching - Results*

Viscosity & Delignification Changes

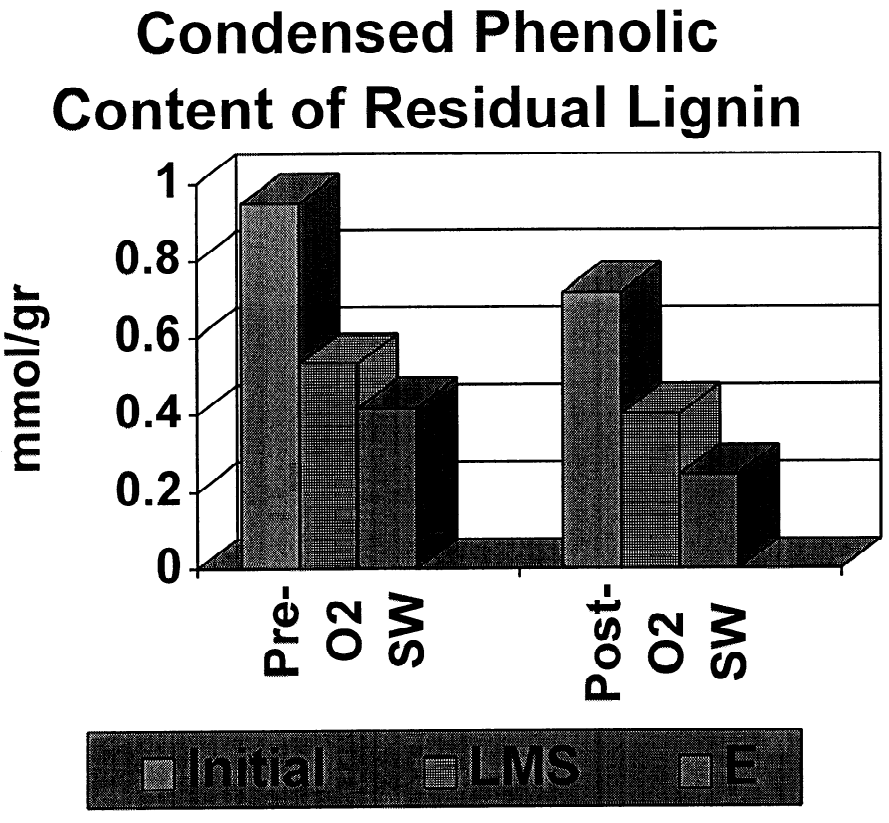


F015: *Bio-assisted Bleaching - Results*



Nitrogen incorporation due to NHB/or laccase

Ph.D. Studies - J. Sealey
Laccase Bio-assisted Bleaching

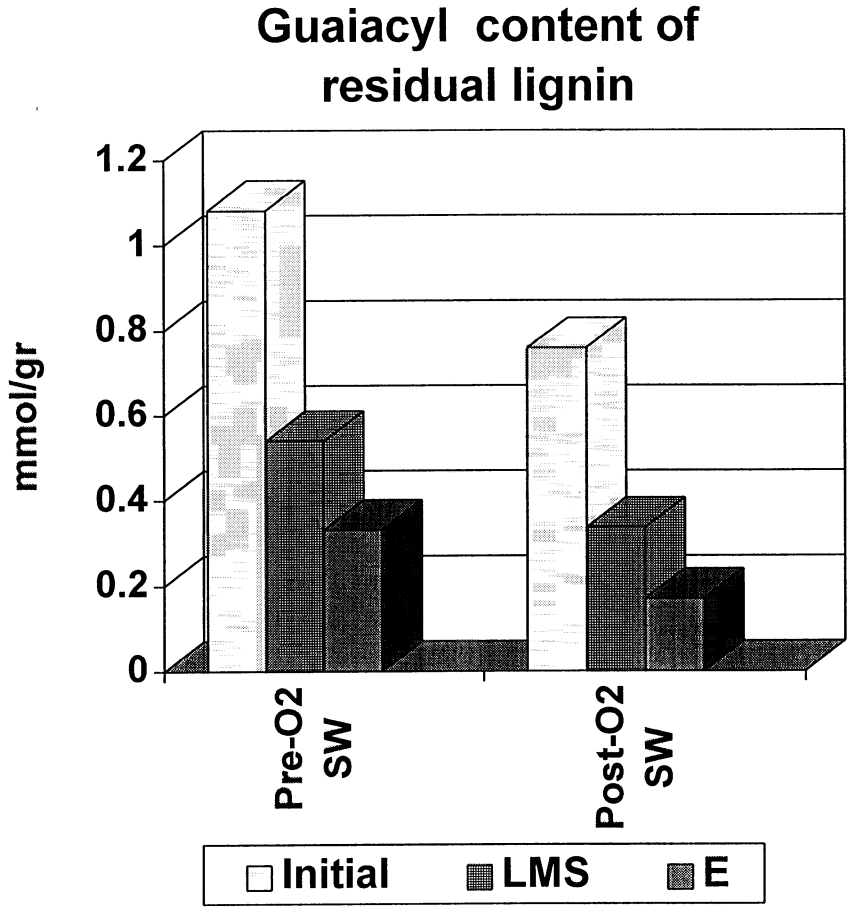


LMS treatment

Significant loss of condensed phenolics

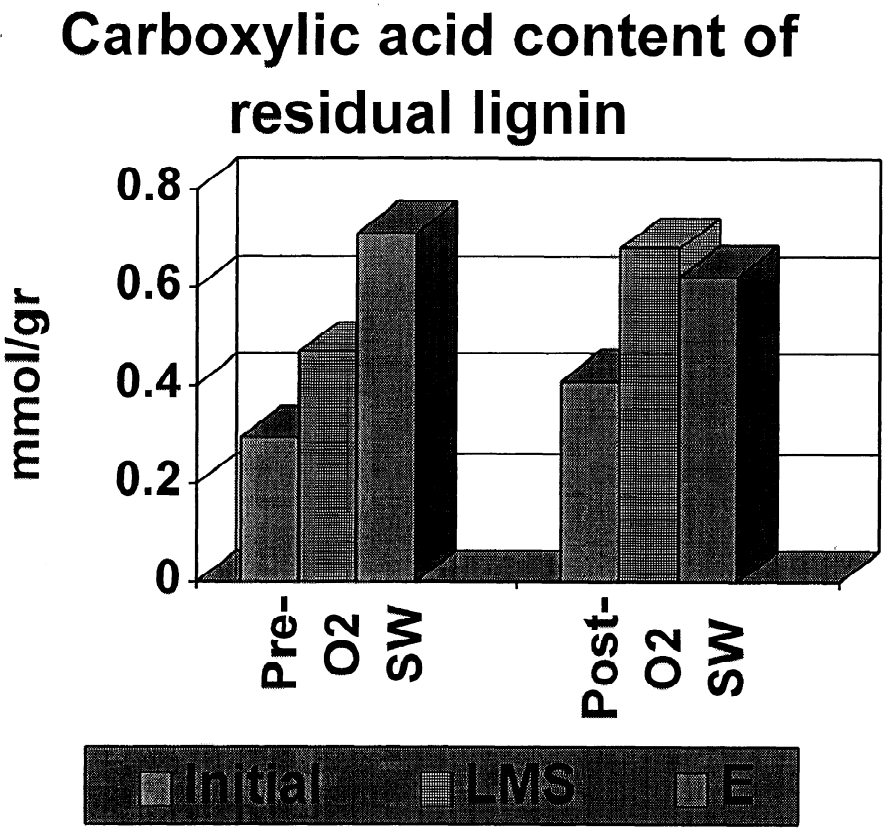
Note: Post-O2 SW & Pre-O2(LMS)E at same kappa # - 17.2

Ph.D. Studies - J. Sealey
Laccase Bio-assisted Bleaching



LMS treatment significantly removes guaiacyl units

Ph.D. Studies - J. Sealey
Laccase Bio-assisted Bleaching



LMS treatment

Significant generation of acids

Laccase Bleaching Studies

Summary

- LMS not sensitive to metals
- Excellent selectivity
- N-incorporation
- Extensive removal of PhOH units
- Residual enriched in acids
- Residual lignin further oxidized than O2

F015: Bio-assisted Bleaching -Future Studies

- Examine chemistry of NHB in LMS bleaching.
- Study LMS:pulp interactions
- Screen kraft pulps for hexenuronic acids
- Chemistry of hexenuronic acids

ACKNOWLEDGMENTS

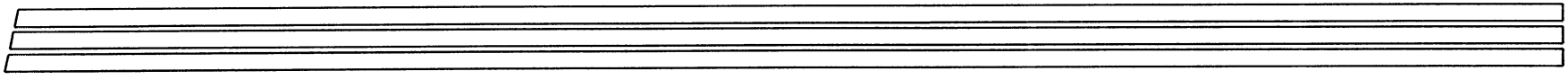
Member Companies of IPST

IPST Analytical Group

L. Allison

P. Froass

J. Sealey



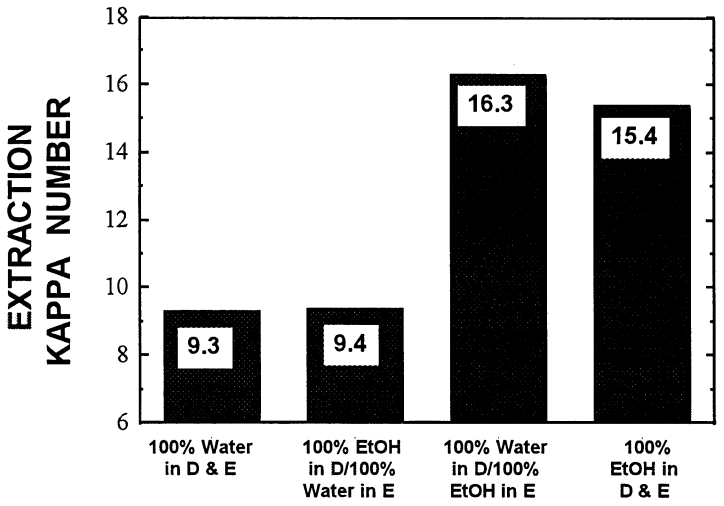
The Influence of Selected Organic Solvents on Chlorine Dioxide and Ozone Pulp Bleaching

Brian N. Brogdon
A490 Thesis Research
to the
Chemical Pulping and Bleaching
Project Advisory Committee
March 20, 1996

Goals of this Research

- **Investigate how select organic solvents/water solutions affect the dissolution of lignin during the early stages of bleaching**
- **Evaluate how changes in fiber swelling affects bleaching delignification**
- **Determine if changes in the bleaching medium can improve bleaching selectivity**

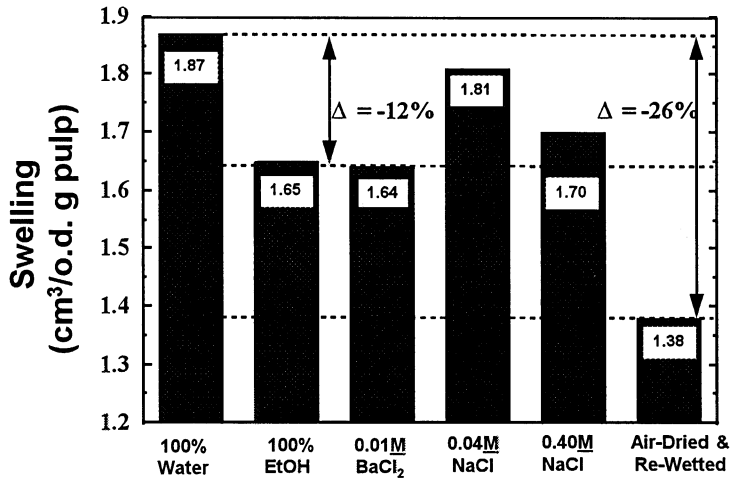
Past Research Results: Influence of Ethanol in the DE Sequence



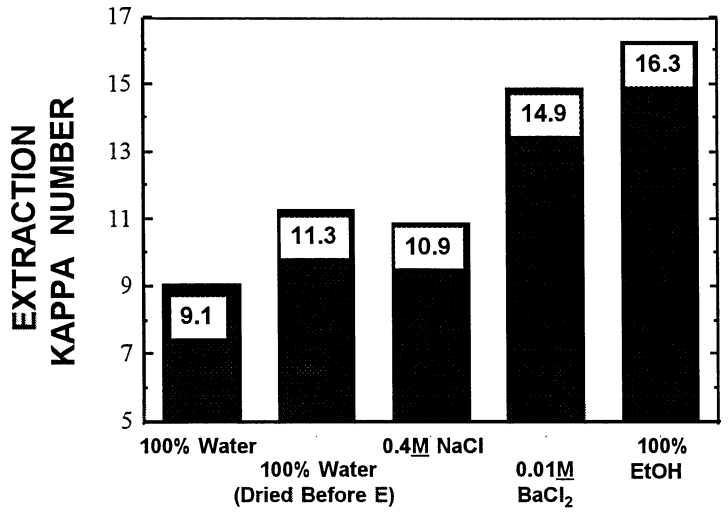
Testing the Swelling Hypothesis

- See if other de-swelling media cause the same decrease in delignification efficiency in the E stage:
  - $BaCl_2$
  - NaCl
- See if fiber de-swelling by air-drying prior to extraction causes decreased delignification in E stage
- See if the oxidized lignin diffusion coefficient is substantially reduced in de-swelling media vs. a swelling medium

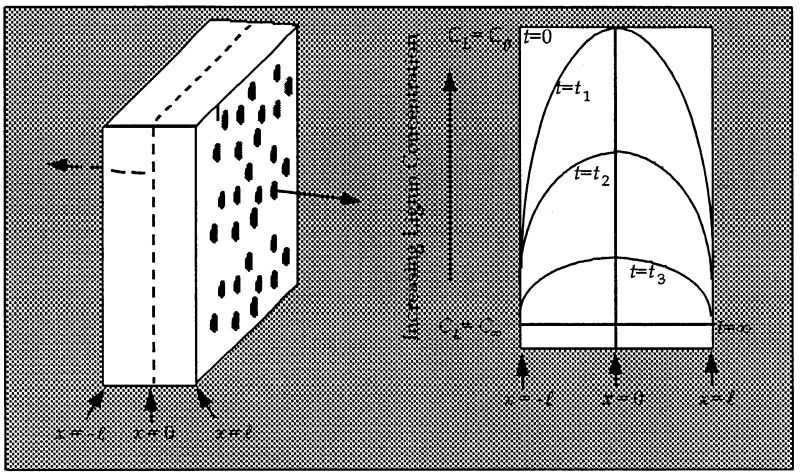
Past Research Results: Fiber Swelling in Various Media



Past Research Results: E Stage Delignification Efficiency in Various Media

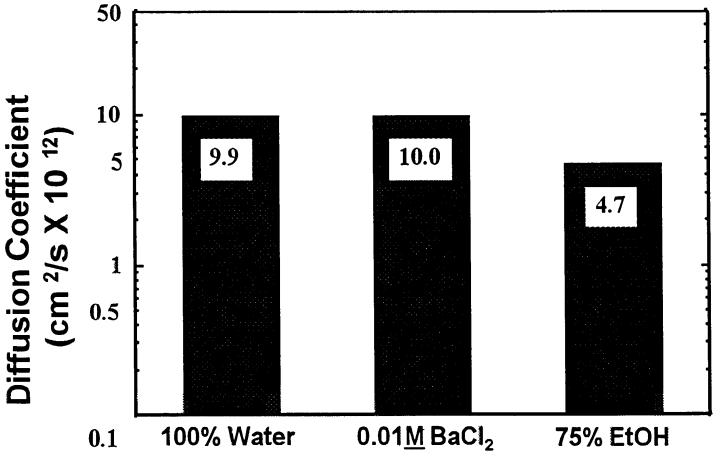


Determination of the Diffusion Coefficient (*D*): Porous Flat Plate Model



B. Favis, PhD Thesis, Montreal, 1981

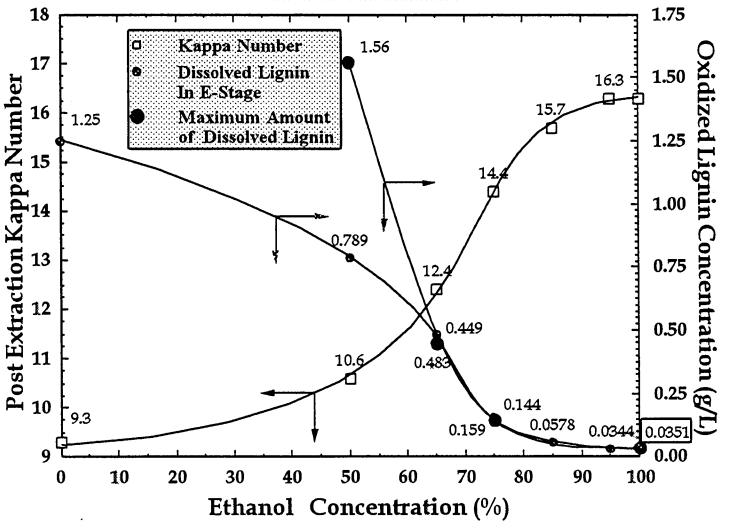
Determination of the Diffusion Coefficient (*D*): Various Extraction Media



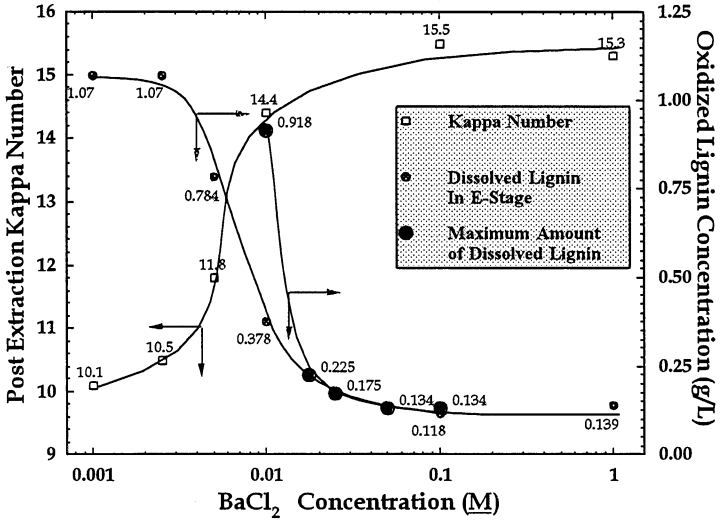
Summary of the Swelling Hypothesis

- **Fiber de-swelling/lignin entrapment hypothesis is unable to explain the experimental results for the various media (delignification performance & diffusion coefficient)**
- **Possible reasons for the hypothesis failure:**
  - **These fragments have MW's 30 -20,000; the sizes of these fragments (1.1-4.2 nm) are much smaller than the pore sizes on the fiber (weight average ~ 6.0 nm)**
  - **Minor changes in fiber pore size (shrinking ~3-7%) will have minimum influence on the diffusion coefficient**

Oxidized Lignin Solubility and Delignification Performance: Ethanol-Water Solutions



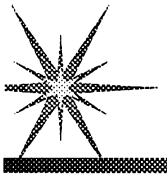
Oxidized Lignin Solubility and Delignification Performance: $BaCl_2$ Solutions



Solubility of Select Carboxylic Acids/Na Salts in Water and Ethanol

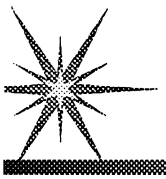
Carboxylic Form	Solubility in g/L			
	Water		Ethanol	
	-COOH	-COONa	-COOH	-COONa
Formic	miscible	769	miscible	sl. sol.
Benzoic	16.6	556	435	13.3
Salicylic	2.2	1110	370	109
Oxalic	143	37	400	insol.
Succinic	77.9	200g/L	54.1	insol.

The Merck Index, 10th Ed. (1983)



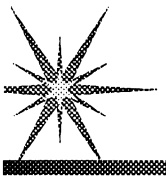
Recent Research Results

- Examine high concentrations of ethanol in the D stage (~90%)
- Examine acid "leaching" of D stage treated pulps
- Preliminary Results:
  - D Stage (27 kappa softwood kraft pulp; ~0.16 KF)
    - Aqueous D stage exit kappa of 16.1
    - 90% EtOH D stage exit kappa of 14.7
  - Acid "leaching" (initial 19.3 kappa)
    - Aqueous leaching exit kappa 18.1
    - 90% EtOH leaching exit kappa 15.1



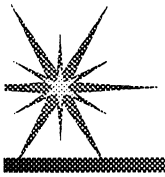
Conclusions

- Use of ethanol-water media for a DE bleaching sequence has mixed results
  - Possibly helps the solubilization of oxidized lignin in D Stage
  - Hinders oxidized lignin solubilization in E stage
- Oxidized lignin solubility is a significant factor to consider with an "Organosolv Bleaching" sequence
- Fiber de-swelling/lignin entrapment caused by a solvent-water medium appears to have little influence on delignification performance



Acknowledgments

- **Thesis Advisory Committee**
  - **Dr. Donald R. Dimmel (Co-Advisor)**
  - **Dr. Thomas J. McDonough (Co-Advisor)**
  - **Dr. Patrick S. Bryant**
- **Dr. Alan W. Rudie for insightful discussions related to this research**



Project F013

Environmentally Compatible
Production of Bleached
Chemical Pulp

Goals

- Measure bleachability at fixed kappa and use to optimize pulping
- Relate lignin structure to bleachability
- Evaluate rapid D_0 bleaching
- Ozone kinetics for improved selectivity
- Delignification and pulp properties
- Toxicity of C- vs. D- effluents

Defining Bleachability

- Ease of removal of lignin under a specified set of conditions from pulp of a *given kappa number*
- Determined by *character* of lignin, as opposed to *amount* of lignin in the pulp

Measuring Bleachability

Measuring Bleachability

- Full sequence bleaching, with measurement of chemical consumption for a given final brightness
- Partial sequence bleaching with some measurement that can serve as a predictor of full-sequence bleachability
- Measurement of a pulp property that correlates with full-sequence bleachability

Candidate Bleachability Measures in D_0(EOP) and D_0E Sequences

- Measurements after the D_0 stage
  - Residual
  - Kappa No.
  - Delignification
  - Brightness
- Measurements after D_0(EOP) or D_0E
  - Kappa no.
  - Delignification
  - Brightness
  - Brightness Increase

Candidate Bleachability Measures in $D_0(EOP)D_1$ and D_0ED_1 Sequences

- End-of-sequence measurements
  - Brightness with 0.25% ClO_2 in D_1
  - Brightness with 0.50% ClO_2 in D_1
  - Brightness with 1.00% ClO_2 in D_1
  - Brightness increments per incremental ClO_2 addition

Assessing D_0 Stage Residual as a Bleachability Predictor

	Kappa Factor	
	0.05	0.20
Mean Resid., Kraft	0.017	0.055
" " ASAQ	0.025	0.125
t-Statistic	-1.5	-9.9
Confidence Level	<95	99.5
pα	<1.3	2.3

Potentially Useful Measures of ECF Bleachability

	Kraft	ASAQ	pα
High KF D_0 Resid.	0.055	0.125	2.3
Low KF D_0 Delig., %	9.0	17.1	2.7
High NaOH D_0E Delig., %	65	73	2.5

ECF Bleachability Hypothesis

- Changing the pulping conditions used to reach a given unbleached kappa number can:
  - change the kinetics of the reaction of the residual lignin with ClO_2 and
  - change the course and stoichiometry of the reaction

Plans: Measuring Bleachability

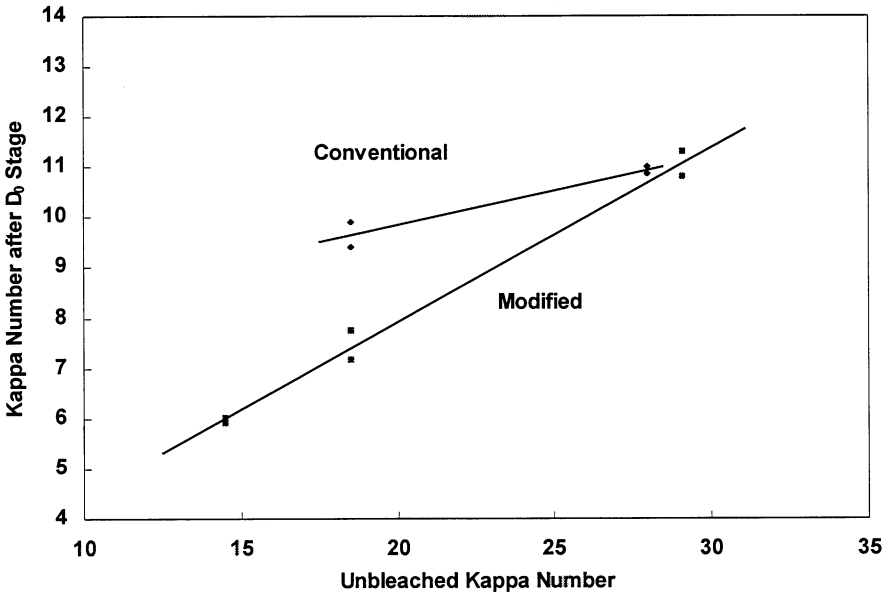
- Select conditions for, and prepare, pulps of widely differing bleachability
- Optimize ECF bleaching of each and quantify bleachability
- Correlate with predictors
- Identify new predictors (rate and stoichiometry parameters, residual lignin structural indicators)

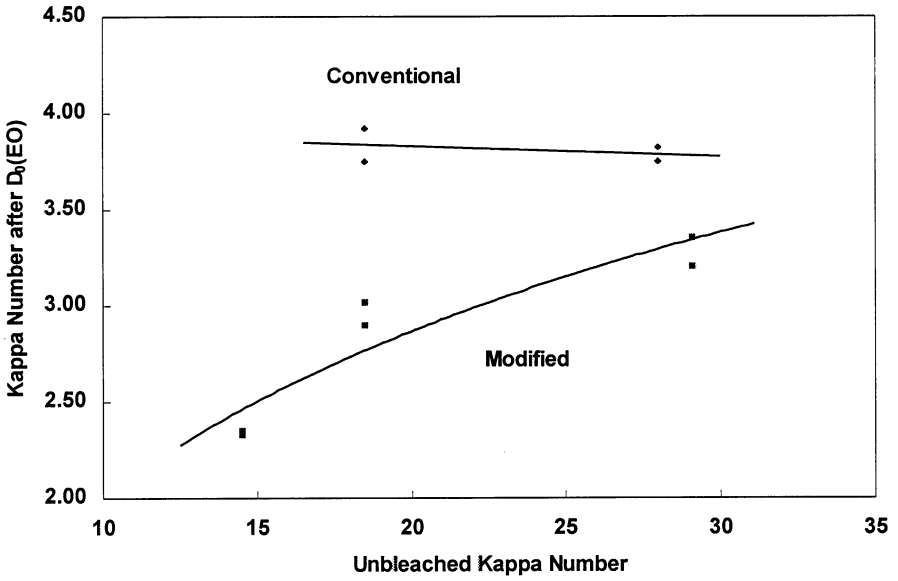
Bleachability Differences Between Different Kraft Pulp Types

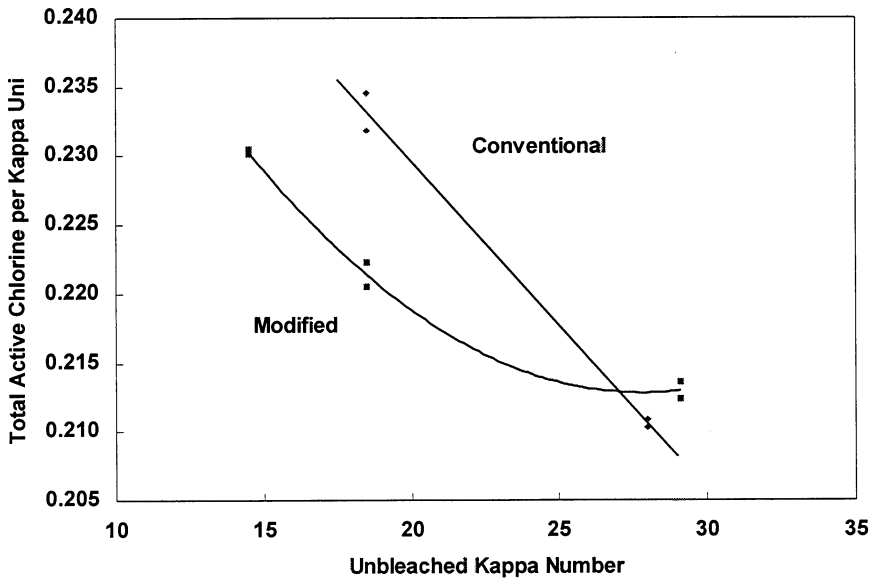
Conventional vs. EMCC®

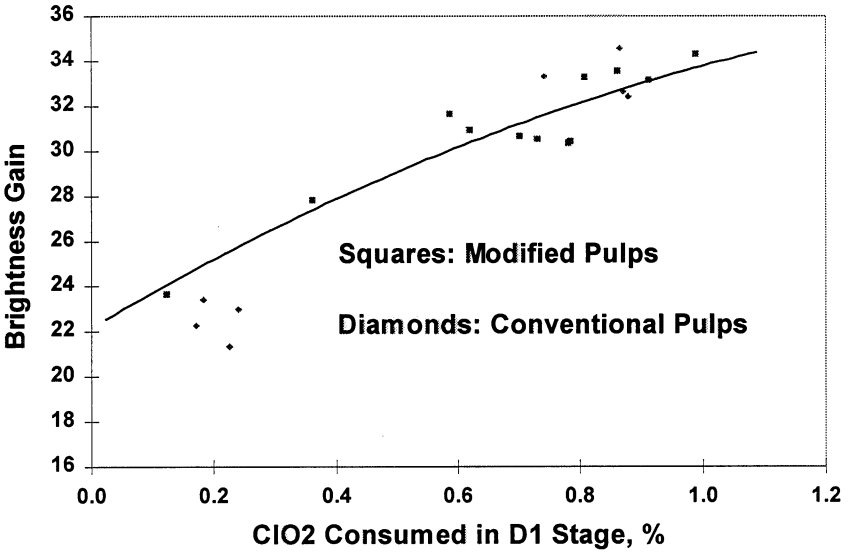
Pulps Investigated

- Conventional Kraft
  - C28
  - C18
- Simulated EMCC
  - E29
  - E18
  - E14



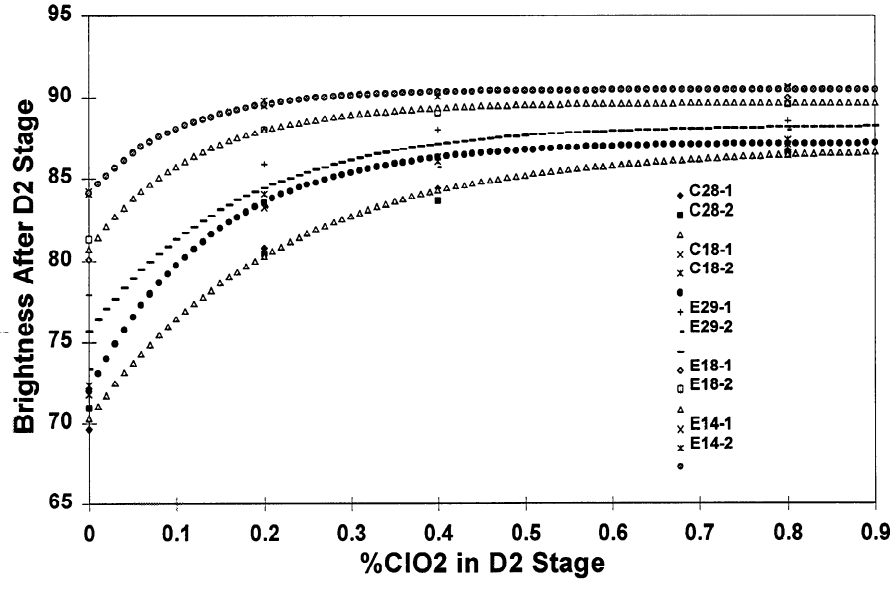

4.50
4.00
3.50
3.00
2.50
2.00
Kappa Number after D_0(EO)
Conventional
Modified
10
15
20
25
30
35
Unbleached Kappa Number


0.240
0.235
0.230
0.225
0.220
0.215
0.210
0.205
Total Active Chlorine per Kappa Uni
Conventional
Modified
10
15
20
25
30
35
Unbleached Kappa Number



$$y = b_0 + b_1\left[1 - \exp\left(-b_2 x\right)\right].$$

y	=	*brightness after D_2*
x	=	*ClO_2 charge in D_2*
b_0	=	*brightness entering D_2*
b_1	=	*maximum brightness gain in D_2*
$b_0 + b_1$	=	*brightness ceiling for given D_1 ClO_2 charge*
b_2	=	*D_2 response factor characterizing rate of approach to brightness ceiling as ClO_2 charge is increased*



Bleachability: Kappa 28-29 Pulps

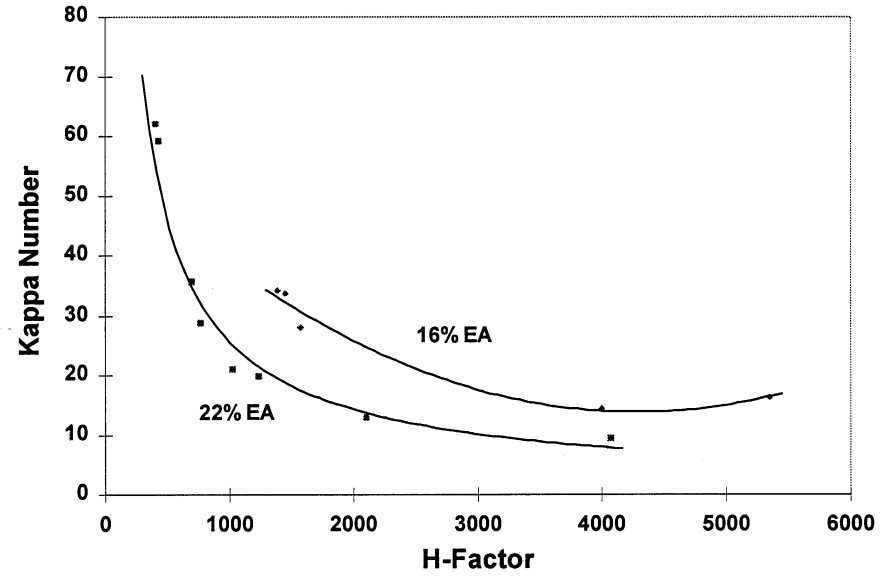
	Conventional	EMCC®
(EO) Kappa	3.8	3.3
Brightness Ceiling	89.0	89.9
Total Kappa Factor (88 Brightness)	0.340	0.324

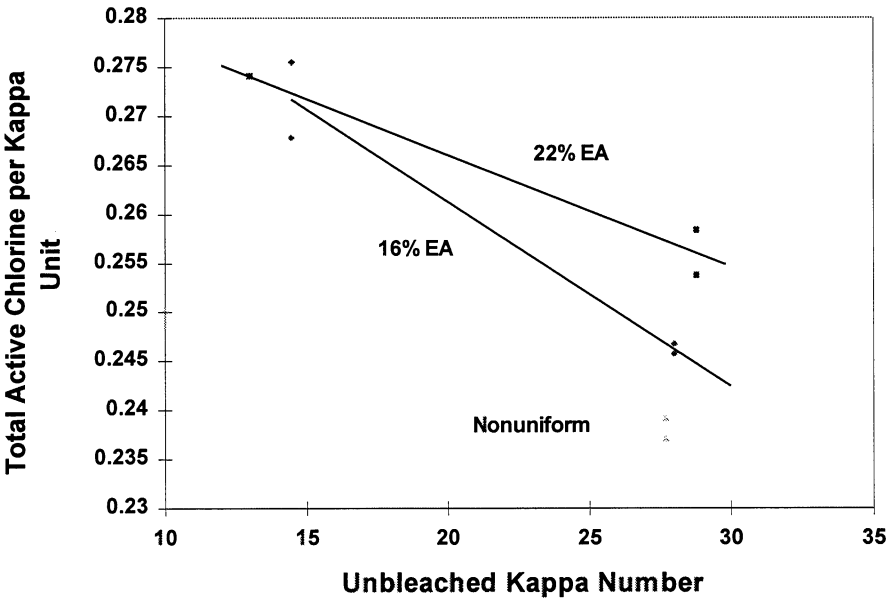
Bleachability: Kappa 18 Pulps

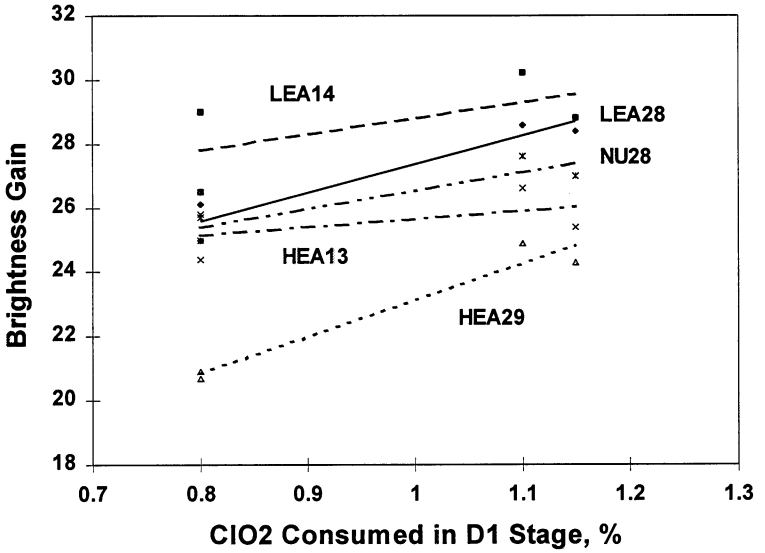
	Conventional	EMCC®
(EO) Kappa	3.8	3.0
Brightness Ceiling	88.7	90.2
Total Kappa Factor (88 Brightness)	0.399	0.342

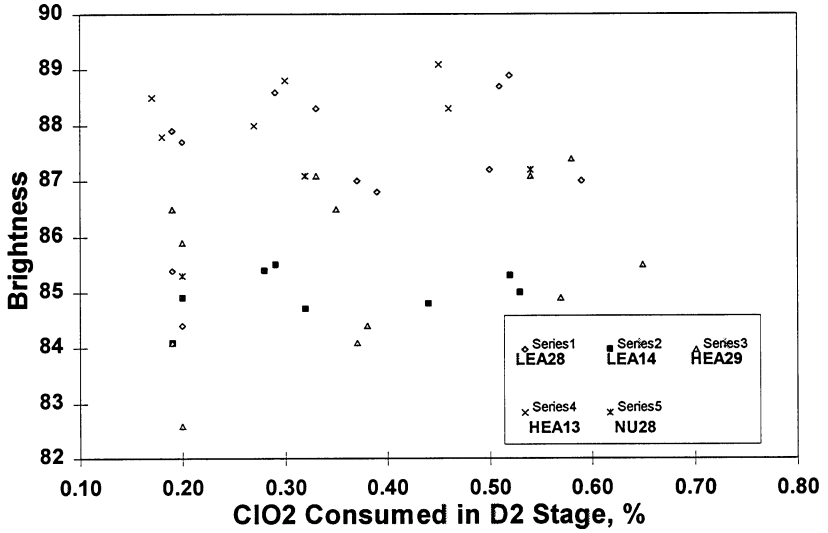
Summary - Bleachability Differences Between Different Kraft Pulp Types

- At a given unbleached kappa number:
  - EMCC is more readily delignified in D(EO)
  - EMCC has higher brightness ceiling
  - EMCC consumes less chemical overall


Kappa Number
H-Factor
16% EA
22% EA
0
10
20
30
40
50
60
70
80
0
1000
2000
3000
4000
5000
6000


Total Active Chlorine per Kappa Unit
Unbleached Kappa Number
22% EA
16% EA
Nonuniform
0.23
0.235
0.24
0.245
0.25
0.255
0.26
0.265
0.27
0.275
0.28
10
15
20
25
30
35


Brightness Gain
32
30
28
26
24
22
20
18
0.7
0.8
0.9
1
1.1
1.2
1.3
LEA14
LEA28
NU28
HEA13
HEA29
ClO2 Consumed in D1 Stage, %


Brightness
90
89
88
87
86
85
84
83
82
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Series1
LEA28
Series2
LEA14
Series3
HEA29
Series4
HEA13
Series5
NU28
ClO2 Consumed in D2 Stage, %

Summary: Effects of Effective Alkali and H-Factor on Bleachability

- Increasing EA at high UK increases specific chemical consumption in D_0(EO) suggesting that low H contributes to poor bleachability
- Low EA pulps have lower brightness but better response in D_1
- Increasing EA at low UK sharply improved D_2 response; low EA, low UK pulps respond poorly
- Increasing EA at high UK worsens D_2 response

Pulping and Bleachability Hypotheses

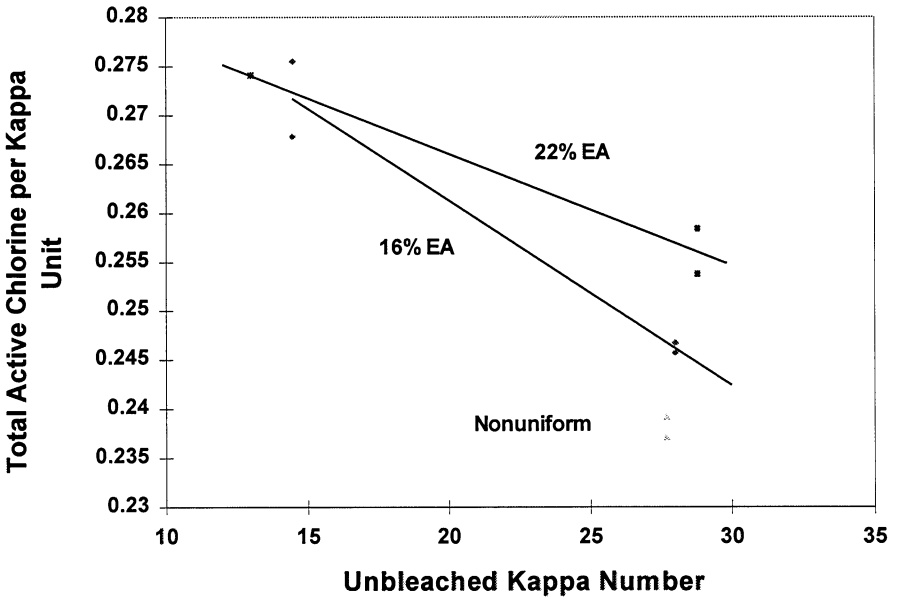
①There exist structural features of residual lignin that beneficially affect bleachability

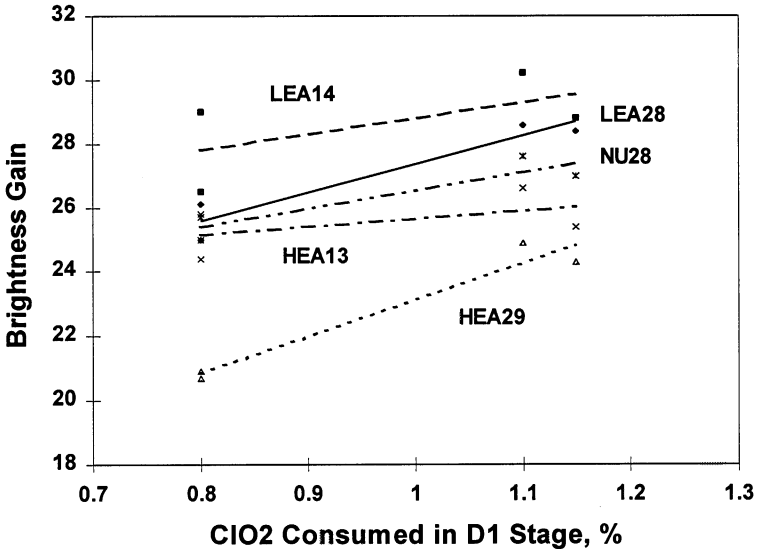
②These features may be created or destroyed in reactions whose rates may be beneficially altered by controlling pulping conditions

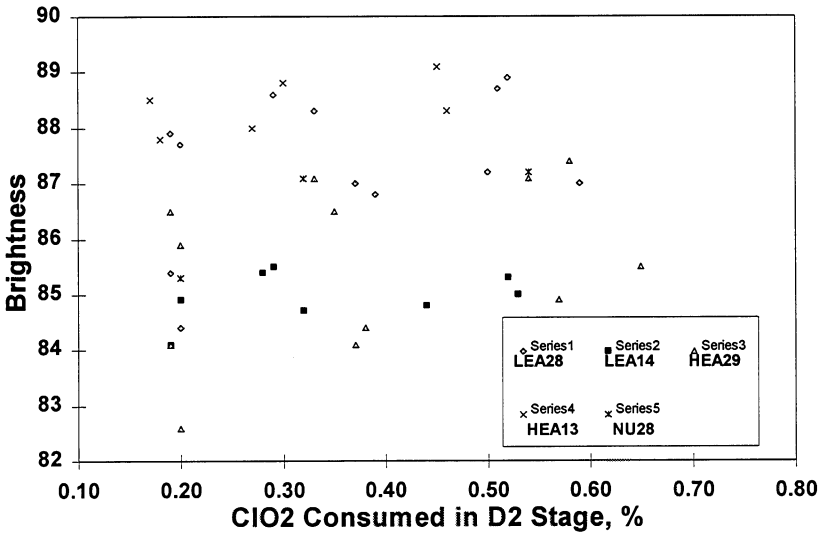
③These features include phenolic hydroxyls, interunit ether linkages, and carboxyls

④The brightness ceiling is due to structures whose formation can be controlled during pulping

Effects of Pulp Uniformity on Bleachability




Brightness Gain
32
30
28
26
24
22
20
18
0.7
0.8
0.9
1
1.1
1.2
1.3
LEA14
LEA28
NU28
HEA13
HEA29
ClO2 Consumed in D1 Stage, %


Brightness
90
89
88
87
86
85
84
83
82
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Series1
LEA28
Series2
LEA14
Series3
HEA29
Series4
HEA13
Series5
NU28
ClO2 Consumed in D2 Stage, %

Summary: Effects of Pulp Uniformity on Bleachability

- Nonuniform pulp is not necessarily more difficult to bleach then uniform pulp
- More work is needed to confirm this observation, especially bleaching of the pure component pulps of the synthetic nonuniform pulp

Short Retention Time ClO_2 Delignification

"Rapid D_0 Bleaching"

Rapid D_0 Bleaching: Previous Results

- Improvement in amount and character of AOX formed
- Brightness penalty after $OD_0(EOP)D_1$ to approximately 85 brightness is less than 1 point when D_0 KF is 0.10
- There is little need for a D_0 bleach tower if mixing is very good

Rapid D_0 Bleaching: Recent Work

- Effects of D_0 retention time (RT) and KF were studied in full bleaching by $D_0(EOP)D_1(EP)D_2$
- Brightness penalty is about 1 point at 0.1 KF but practically disappears at 0.15 and 0.2 KF
- Modest improvements in AOX and Cl/C

Rapid D_0 Bleaching: Conclusion

- This technology is ready to be tried in the mill

Dues Funded Project F017: Closed Mill Operations

Management of Nonprocess Element

Patrick Bryant	Assistant Professor
Clark Woitkovich	Associate Scientist
Alex Shaket	Technician III

Related Student Research

Eddie Gravely	M.S. Student
Ryan Mills	M.S. Student
Doug Milligan	M.S. Student
Brian Zehner	M.S. Student

Acknowledgments

- IPST Member Companies
- Georgia Pacific
- Union Camp
- Consolidated Papers

Topics

- Overview
- Benefits of carry-over when closing up
- General chemical equilibria model
- Measuring equilibrium constants
- Summary

Keeping the Closed Mill Open and Profitable

- Environmental pressures are forcing mills towards low-effluent operations
- The process technology to achieve low-effluent operations will not be the same for every company or every mill
- Mills need better tools to evaluate their alternatives

Expected Results

- Optimum low-effluent mill design will allow mills to meet their environmental targets and to still be profitable
- IPST's research program will provide member companies with the data and the design tools to implement mill closure

Low-Effluent Mills

- Low-effluent mills reduce fresh water use and its subsequent discharge by reusing water internally within the process
- Reduces pollution load to the environment
- Can result in an increased NPE concentrations

Nonprocess Elements (NPEs)

- Trace contaminants which enter the process primarily with the wood
- Keeping NPEs out of the process is impractical
- Build-up of NPEs can increase manufacturing costs and reduce product quality

IPST Research Program

- Mill studies of NPE behavior
- Lab studies characterizing the behavior of NPE's
- New validated NPE simulation models
- Assist mills in the use of these new simulation tools to implement successful mill closure

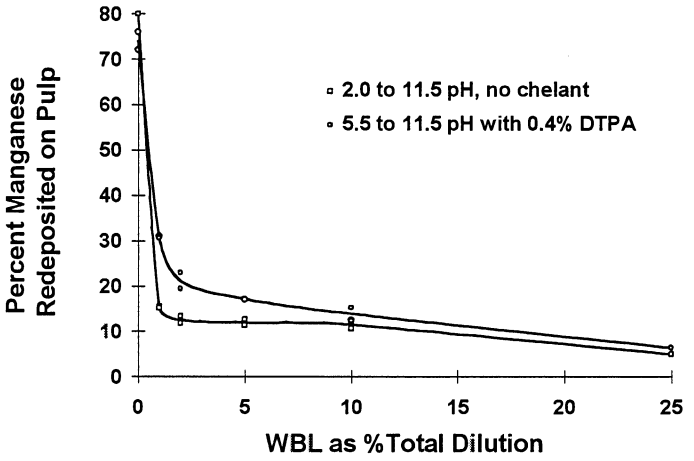
Topics

- Overview
- ➧ Benefits of carry-over when closing up
- General chemical equilibria model
- Measuring equilibrium constants
- Summary

Benefits of Carry-over when Closing the Bleach Plant

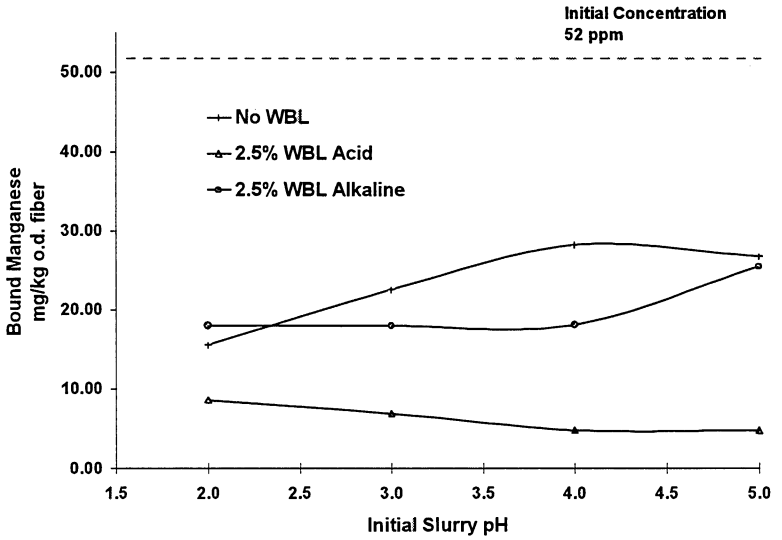
- Carry-over or carry-back of dissolved solids into the A or Q stage improves metals removal
- The concentration of Na in A or Q stage can increase by factor of 30 when closing
- Dissolved organics irreversibly bind to cations under acidic conditions
- Colloidal suspension of organically bound metals follow the filtrate split in washing

Previous Carry-over Studies

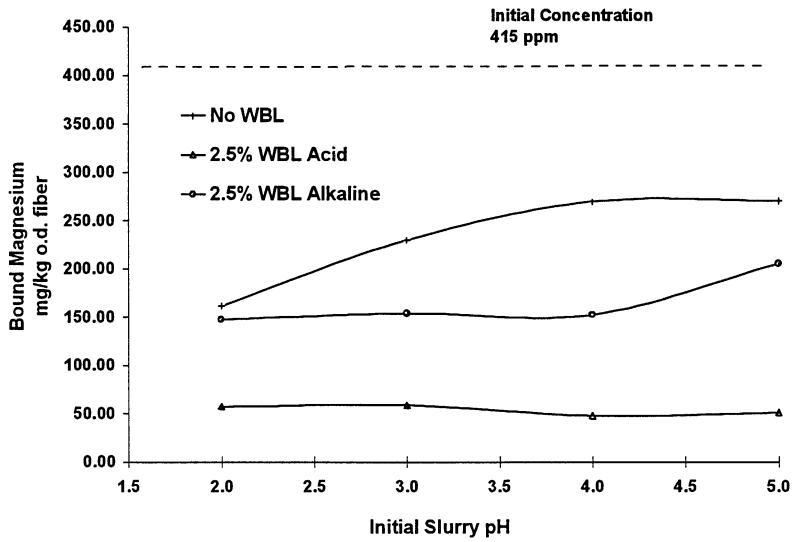


Bryant, P.S. and Edwards, L.L., *Tappi J.*, "Manganese Removal in Closed Kraft Mill Bleach Plants", 77(2), p. 137 (1994).

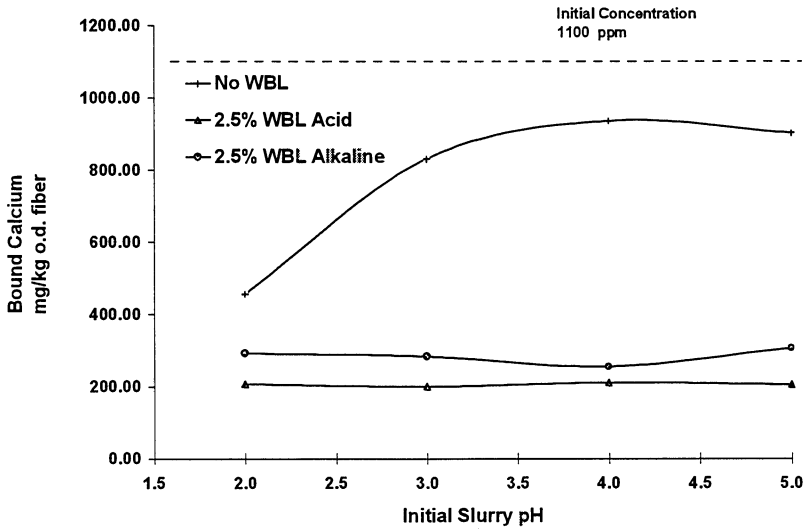
Impact of Carry-over on Mn



Impact of Carry-over on Mg



Impact of Carry-over on Ca



Implications of Carry-over Studies

- Na^+ can be used in place of H^+ to aid in metal removal
- Acidified dissolved organics can be used to "scavenge" cations
- Further studies are needed to determine if "natural partitioning" of metals can be enhanced using this knowledge

Topics

- Overview
- Benefits of carry-over when closing up
- ➡ General chemical equilibria model
- Measuring equilibrium constants
- Summary

Modeling NPE Behavior

- Predicting concentrations of NPEs in process streams by simulation will be an important aspect of designing low-effluent mills
- Previous modeling technology has focused on fiber, process elements and dissolved organics
- Alternative purge levels and process configurations for NPE control are not easily evaluated today

Predictive Equilibrium Model

- Initial beta version of general chemical equilibria model released Fall 1995
- Final release of version 1.0 scheduled for August 1996
- Future version enhancements
  - Improved pulp and DOM formation constants
  - Improved activity coefficient estimations
  - Gas solubility's and Redox reactions

Topics

- Overview
- Benefits of carry-over when closing up
- General chemical equilibria model
- ➧ Measuring equilibrium constants
- Summary

Measurement of Pulp/Cation Equilibrium Constants

- Previously, pulp/cation equilibrium constants have been "tuned" using data from multi-component sorption experiments
- New student studies are underway to develop a technique that will determine binary system equilibrium constants
  - ➢ Eddie Gravely, first year M.S. student
- Sensitivity of the equilibrium constants to commercial pulp properties and to physical properties of the slurry will be evaluated

Measurement of Pulp/Cation Equilibrium Constants

- Determination of equilibrium constants by single cation titration
- Measurement of pulp binding sites by conductometric titration
- Measurement of unbound cations by ion selective probes
- Calculation of bound cations by mass balance

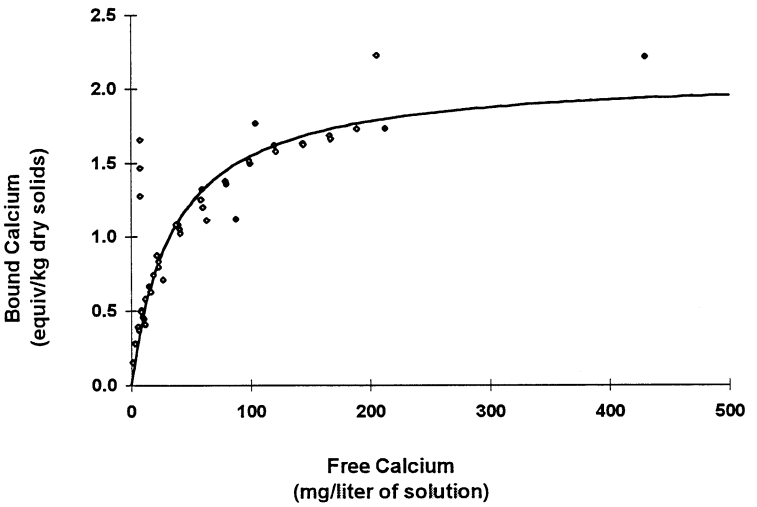
Measurement of DOM/Cation Equilibrium Constants

- Student studies are underway to develop a technique that will determine binary system equilibrium constants
  - ➢ Ryan Mills second year M.S. student
- Determination of DOM/cation equilibrium constants is difficult
- pH must remain high or lignin will precipitate
- Separation of bound cations from free not possible

Measurement of DOM/Cation Equilibrium Constants

- WBL is pretreated with a ion-exchange resin to remove all cations except Na^+ and H^+
- Determination of equilibrium constants by single cation titration
- Measurement of unbound cations by ion selective probes
- Measurement of bound cations and total binding site by mass balance

Calcium Bound to DOM in WBL



Topics

- Overview
- Benefits of carry-over when closing up
- General chemical equilibria model
- Measuring equilibrium constants
- ➧ Summary

Summary

- NPE Control Technology is Required to Achieve Significant Mill Closure
- Understanding NPE Behavior Within the Pulp and Paper Mill is Key to Their Management and Control
- IPST Has a Strong Research Program in Place that Will Provide Member Companies With Data and Process Design Tools to Evaluate Mill Closure

Project F017

Novel Metals Management Methods With an Emphasis on Iron

Annual Project Review:
March 20, 1996

Project Staff

Alan Rudie

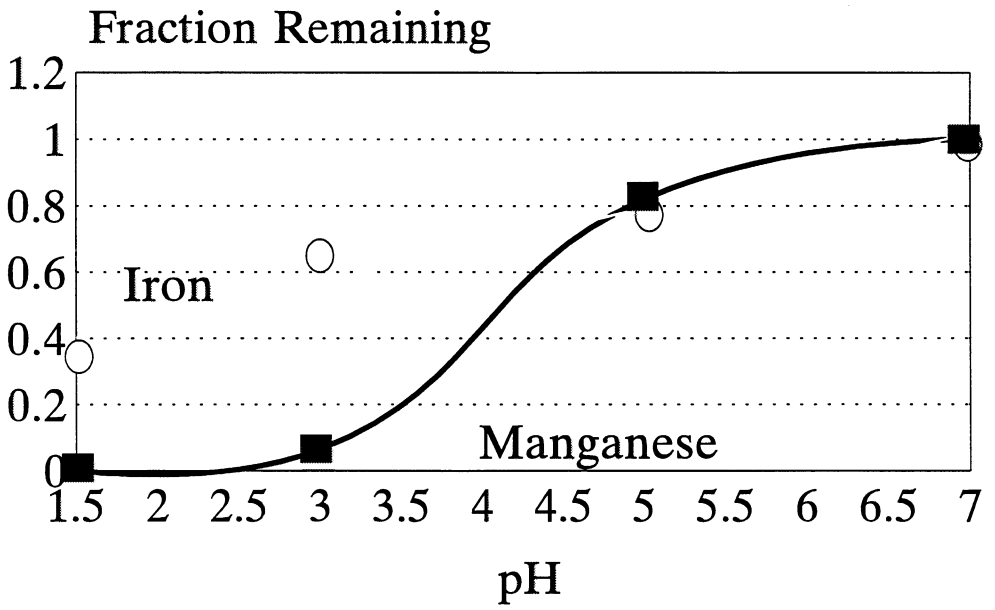
Fadi Chakar, M.S. 1995
(Independent Study, Lab)

Giselle Ow Yang,
M.S. Candidate, 1996.

Objective:

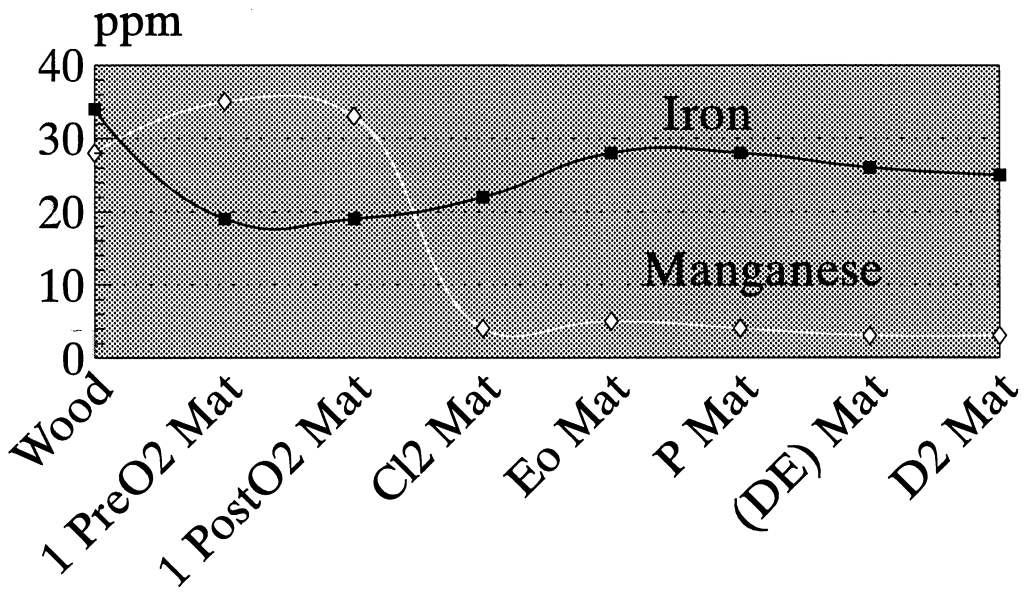
- Evaluate novel metals removal strategies, with an emphasis on improving the removal efficiency of iron.
- Determine the nature of "hard-to-remove" iron in pulp.

Iron and Manganese Removal
Fraction of original metal after treatment



Samples treated with sulfuric acid for 30 minutes and 55°C.

Bleach Plant Metal Profile
OC/DEPDED

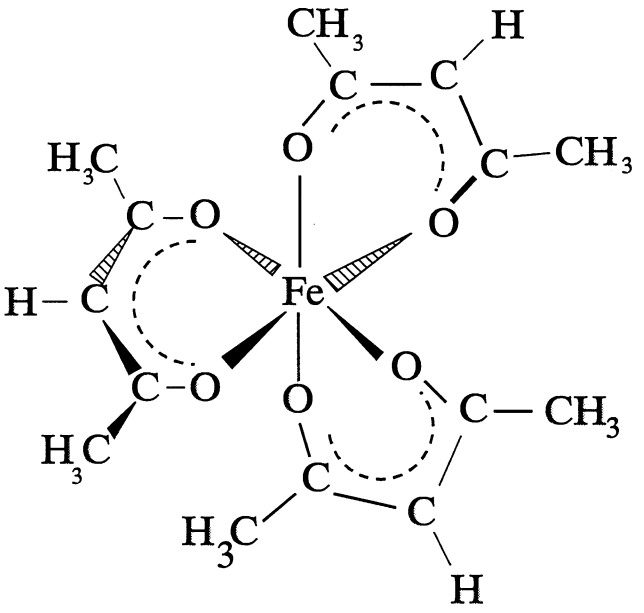


Bryant, P.A., Proceedings, 1994 Int. Non-Chlorine Bleaching Conference

Novel Metals Removal Methods
Fluoride and Acetylacetone

- Fluoride has a high affinity for iron: The stability constant is 10^5 compared to 10^2 for Sulfate, 30 for Chloride and 10^3 for acetate.
- 2,4-pentanedione has an even higher affinity for iron. The stability constant of 10^{11} competes with hydroxide at 10^{12}.

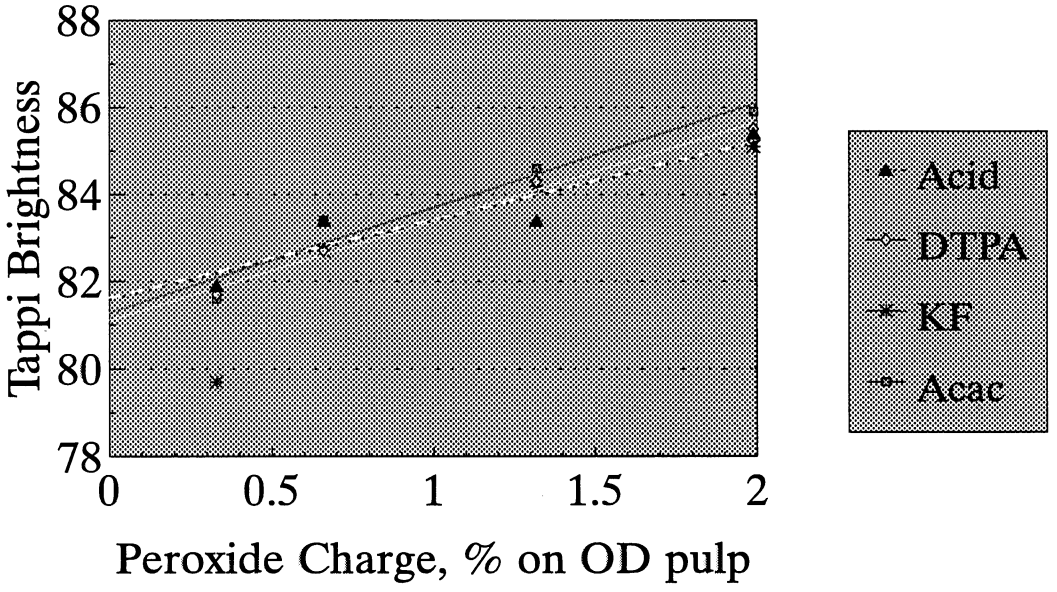
tris(2,4-pentanedione)iron(III)



Evaluation of metals removal using an OZEP bleaching sequence

- Pulps were oxygen bleached to a 10 Kappa.
- Samples were pretreated with acid, acetylacetone, or fluoride.
- Samples were bleached with 0.7% ozone and extracted.
- Samples were final bleached using 4 levels of hydrogen peroxide.

OQZEP Bleaching Results
Using the different metals removal methods.

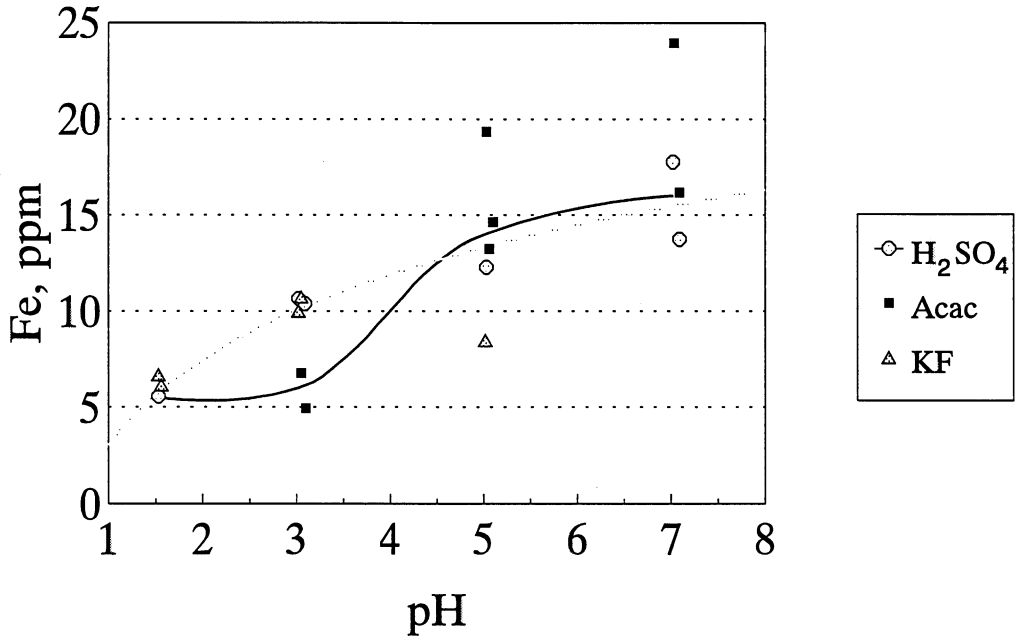


Fadi Chakar, A-280 Pulping and Bleaching Laboratory

Metals Removal Efficiency
Comparison of novel methods to sulfuric acid

- Pulp was treated with acetylacetone or potassium fluoride over a range in pH.
- Results are compared to metals control with sulfuric acid.

Residual Iron on pulp after treatment using the various methods



Evaluation of metals removal by distillation.

- Neutral metal acetylacetonate complexes can be distilled.
- Efficiency of metals removal from filtrates was evaluated by distilling off 1%, 5% and 10% of a sulfuric acid wash filtrate.

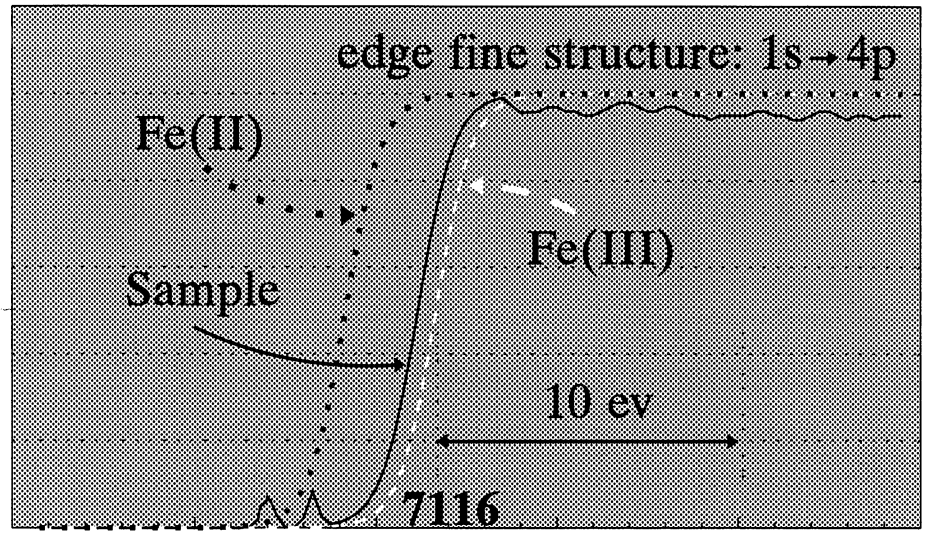
Metals Removal
Concentration in Distillate

ml (%)	Fe	Mn	Cu
5 (1%)	0.5	0	0
25 (5%)	15	0	0.4
50 (10%)	0	0	2.6

X-Ray Spectroscopy

- The K X-ray absorption ejects an electron from the 1s orbital.
- The position of the X-ray edge is sensitive to the oxidation state of the metal. X-ray Absorption Near Edge Spectroscopy (XANES).
- Microprobe can evaluate distribution.
- Other edge features can give structural details.

Simulated XANES Spectra for Iron in Wood Pulp



Pulp samples and results of XANES

Sample	Fe	% removed	XANES ev
Sawdust	~ 35	~ 50%	-1.5
untreated	13	0	-0.5
Acid	10	23	-0.5
DTPA	11	15	-2.0
Fe(II)	standard		-4.5

Conclusions

- Acetylacetone (2,4-pentanedione) can be used to remove iron from wood pulp, but offers little advantage over conventional methods.
- Fluoride ions do not appear to significantly improve iron removal relative to an acid wash.
- Iron acetyacetonate complexes can be distilled from the acid wash filtrates, but the manganese complexes are not volatile.

Recommendations for future work:

- Evaluate methods to distill manganese from acid wash filtrates.
- Continue to evaluate other methods to remove iron from wood pulp.
- Continue X-ray spectroscopy to determine the nature of hard-to-remove iron.

Acknowledgements

We thank Dr. Paul Bertsch and Douglas Hunter of the University of Georgia Savannah River Ecology Laboratory for supplying the XANES spectra, and the member companies for supporting this research.

Sulfur-Free Selective Pulping

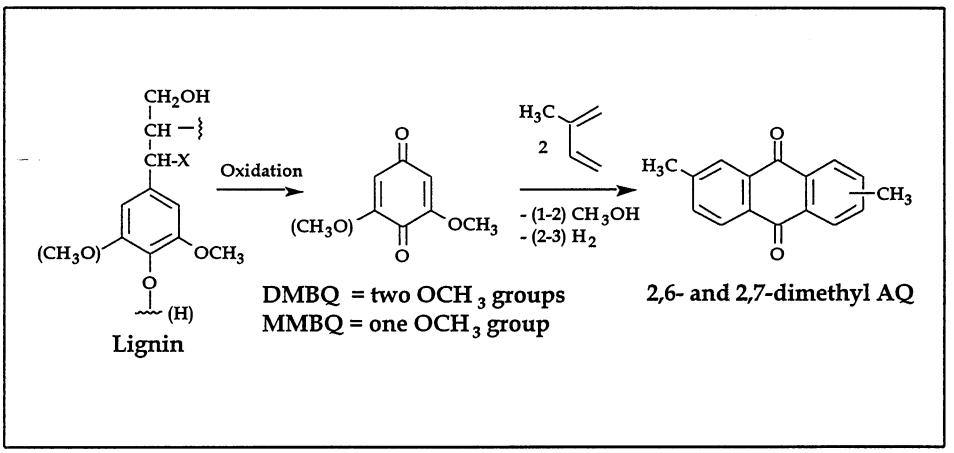
- Project Number: 3661
- FY96-97 Budget: $280,000 (DOE)
- Project Staff: Donald Dimmel, Michael Savidakis
- Ojective: To produce a low-cost catalyst which, when used in pulping systems, will increase pulping rates and yields, while reducing the dependence on sulfur additives. The process is based on the conversion of inexpensive lignin to a useful quinone-type catalyst.

Current Status

- Can Produce ~$3.00/lb Catalyst from Lignin
- Target is ~$1.00/lb
- Principal Cost Factor is the Low Yield of the Catalyst Mixture obtained from Lignin
- Focus has been on Optimization of the Synthesis Yield and Demonstrating the Effectiveness of the Catalyst Mixture in Pulping Studies

Sulfur-Free Selective Pulping

Processing Steps



Sulfur-Free Selective Pulping

NO_2 Oxidation Results

Substrate	Quinone Yield
Hardwood Lignin	5%
Fractionated Hardwood Lignin	10%
CuO Pretreated Hardwood Lignin	15%
Syringyl Monomers	90%
Guaiacyl Monomers	10%

Sulfur-Free Selective Pulping

Approaches to Improved Yields

- Isolate a Lower Molecular Weight Lignin
- Fragmentation of the Lignin Prior to NO_2 Oxidation
- Recycling of NO_2 Oxidation Liquors for Subsequent Oxidations

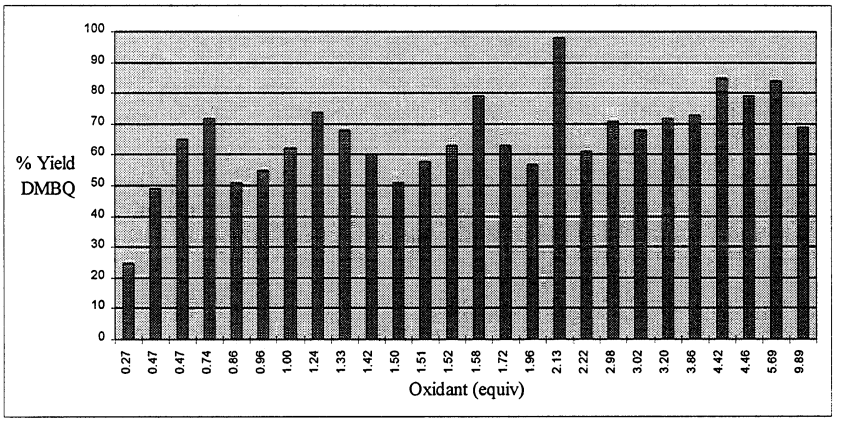
Sulfur-Free Selective Pulping

Recent Research Areas

- Optimization NO_2 Oxidation Yields
- Elucidation of the NO_2 Oxidation Mechanism
- Investigation of Alternative Oxidants for NO_2
- Evaluation of Dissolved Hardwood Lignins from Different Pulping Processes and Times
- Examination of Lignin Fragmentation by Acidolysis, Amines, and Laccase/ABTS
- Evaluation of DMAQ in Pulping Experiments

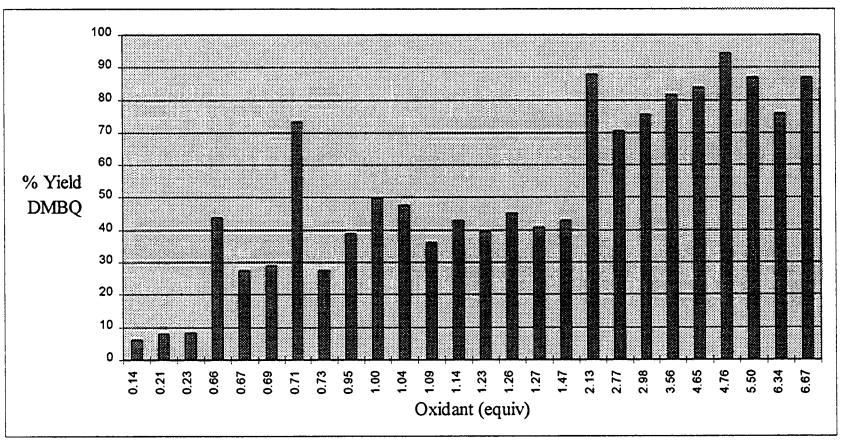
Sulfur-Free Selective Pulping

NO_2 Oxidation of Syringyl alcohol



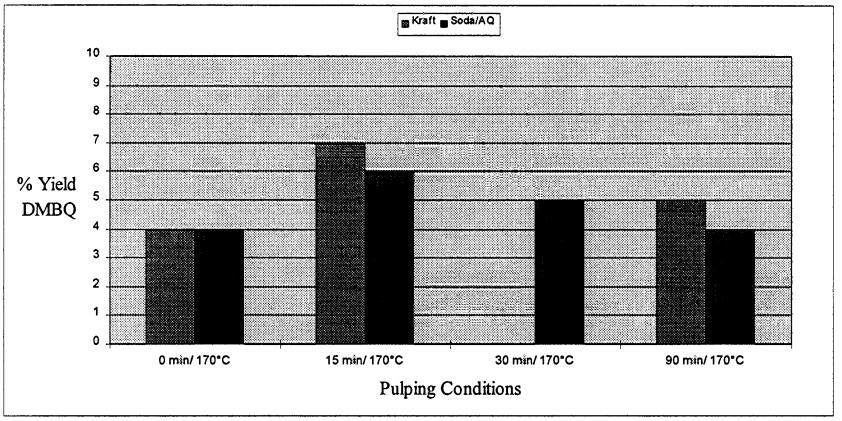
Sulfur-Free Selective Pulping

NO_2 Oxidation of Syringaldehyde



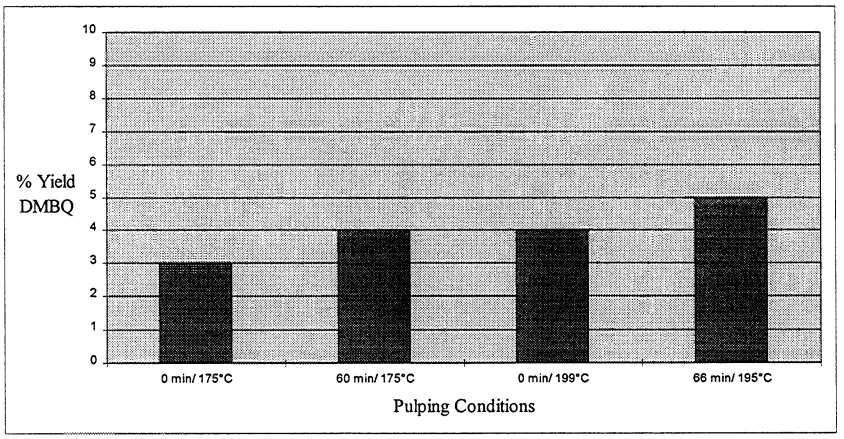
Sulfur-Free Selective Pulping

Oxidation of Kraft and Soda/AQ Lignins



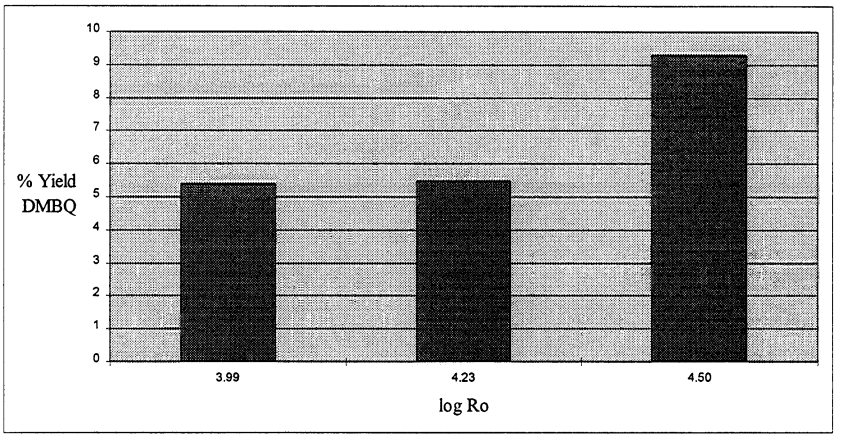
Sulfur-Free Selective Pulping

Oxidation of Organosolv Lignins



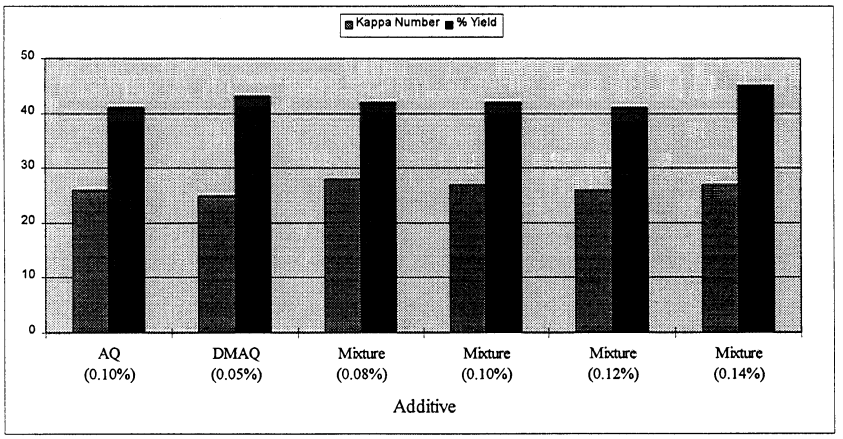
Sulfur-Free Selective Pulping

Oxidation of Steam Exploded Lignins



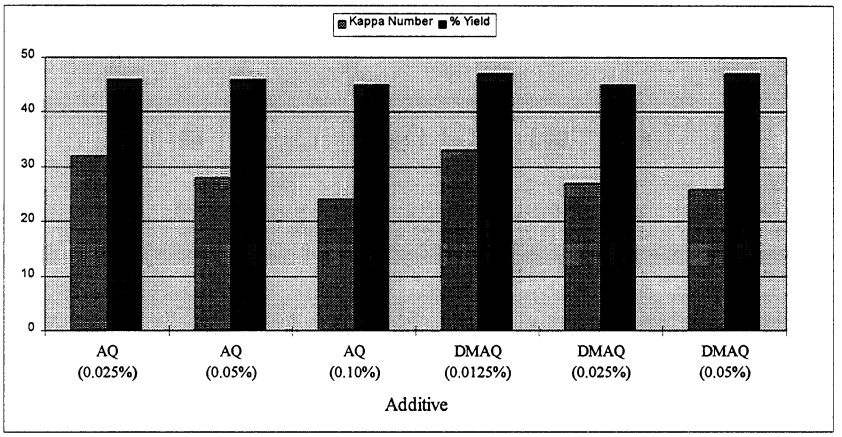
Sulfur-Free Selective Pulping

Soda/Catalyst Pulping



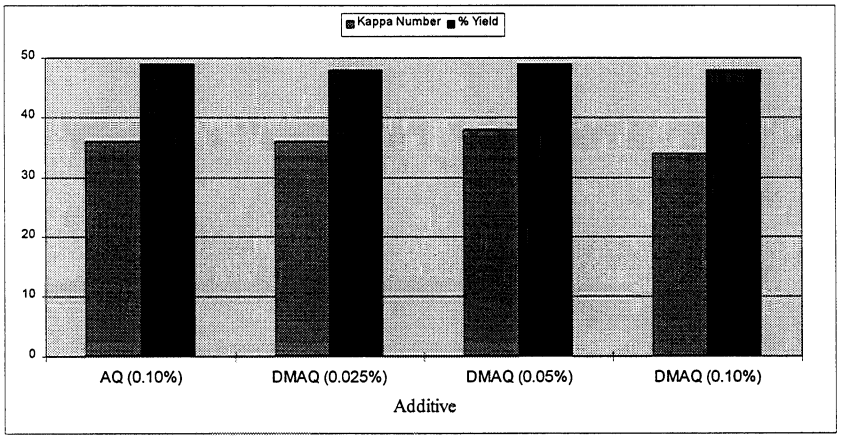
Sulfur-Free Selective Pulping

Kraft/Catalyst Pulping



Sulfur-Free Selective Pulping

Polysulfide/Catalyst Pulping



Sulfur-Free Selective Pulping

Summary

- Lower Molecular Weight Lignins will Reduce the Cost of the Catalyst
- Efficient Lignin Fractionating Techniques are Needed
- DMAQ is Twice as Effective as AQ in Soda/AQ and Kraft/AQ Pulping
- DMAQ may be up to Four Times as Effective as AQ in Polysulfide/AQ Pulping
- Non-DMAQ Catalyst Mixture Components are Inactive

Sulfur-Free Selective Pulping

Future Studies

- Determine the Bleachability and Paper Properties of Catalyst-from-Lignin Pulps
- Assess Catalyst Performance in Ext. Delignification
- Develop Lignin Fragmentation Processes, Including a Catalytic CuO Stage
- Select Diels-Alder Conditions Based on Economic Considerations
- Complete a New Economic Evaluation of the Process

Relationship Between Residual Lignin Structure and Pulp Bleachability

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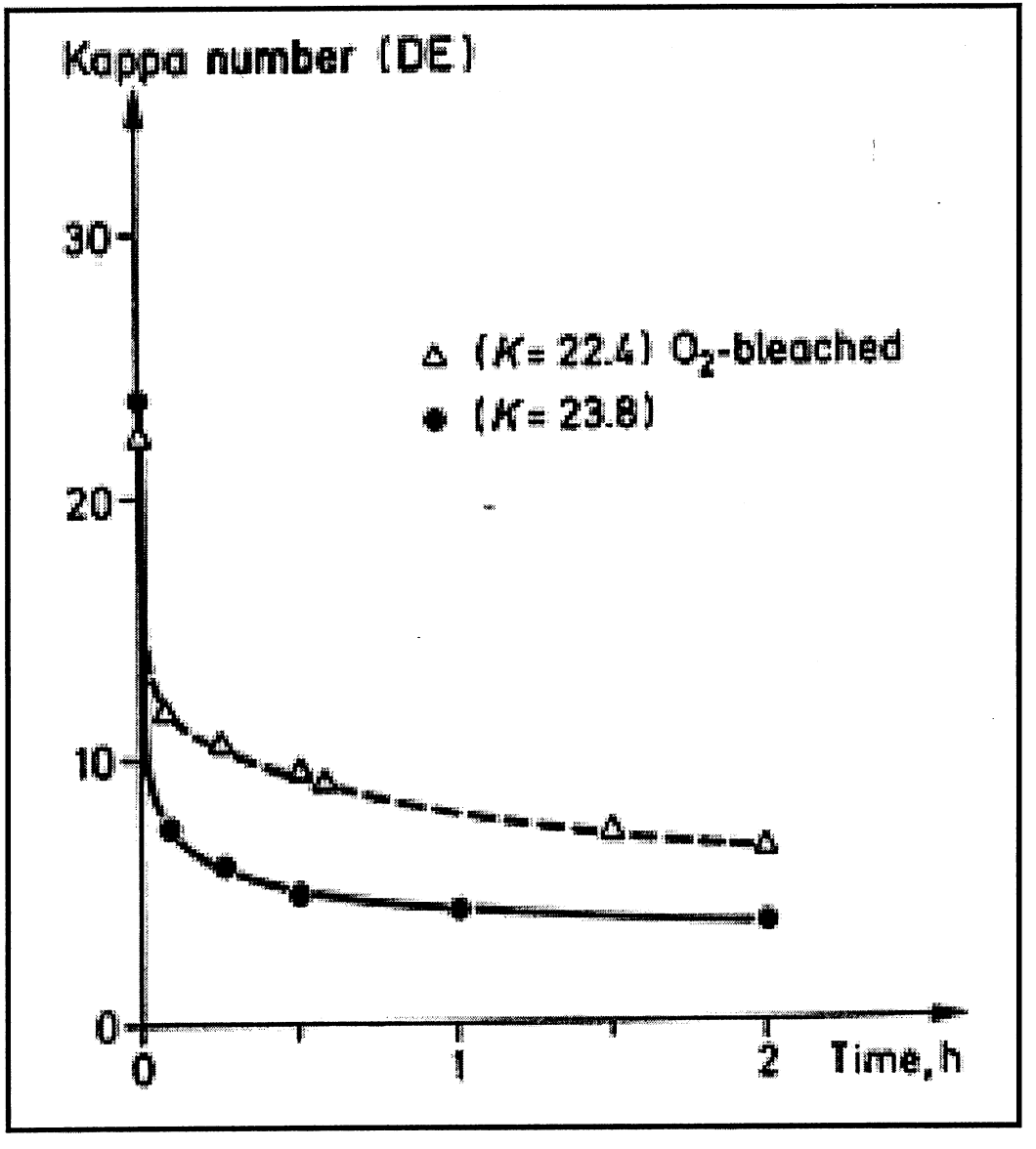
Kamyr, Inc.

Background

- Impact of extended delignification on bleachability employing 100% ClO_2
  - Residual lignin structure is influenced by pulping conditions and the extent of delignification
  - Residual lignin's structure will influence its reactivity towards ClO_2

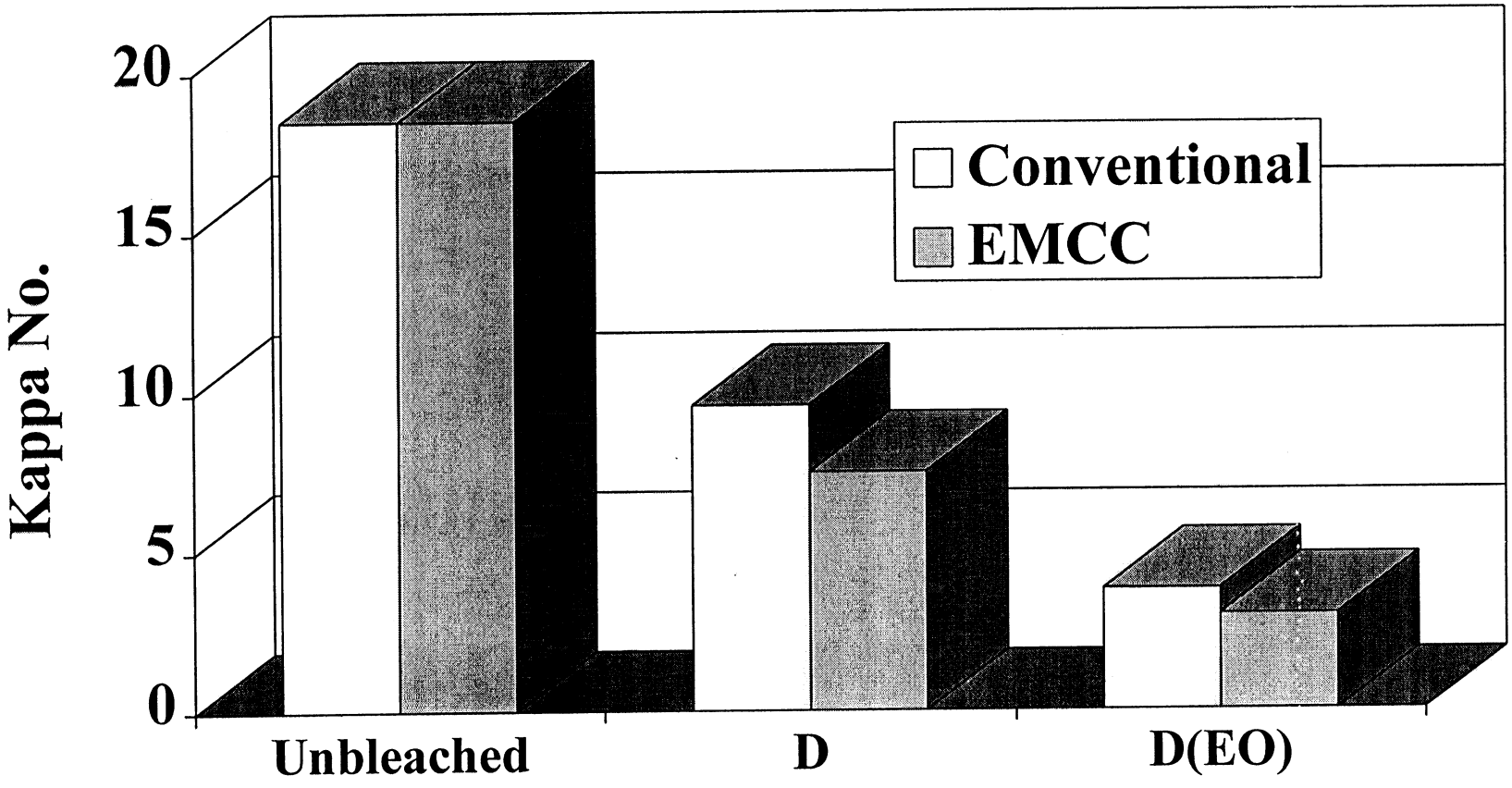
Research Objectives

- Determine how the extent of deligni and pulping process variables affect bleachability in a D(EO) delignifica sequence
- Relate the unbleached residual ligni structure and residual lignin reactivi towards ClO_2 to bleachability



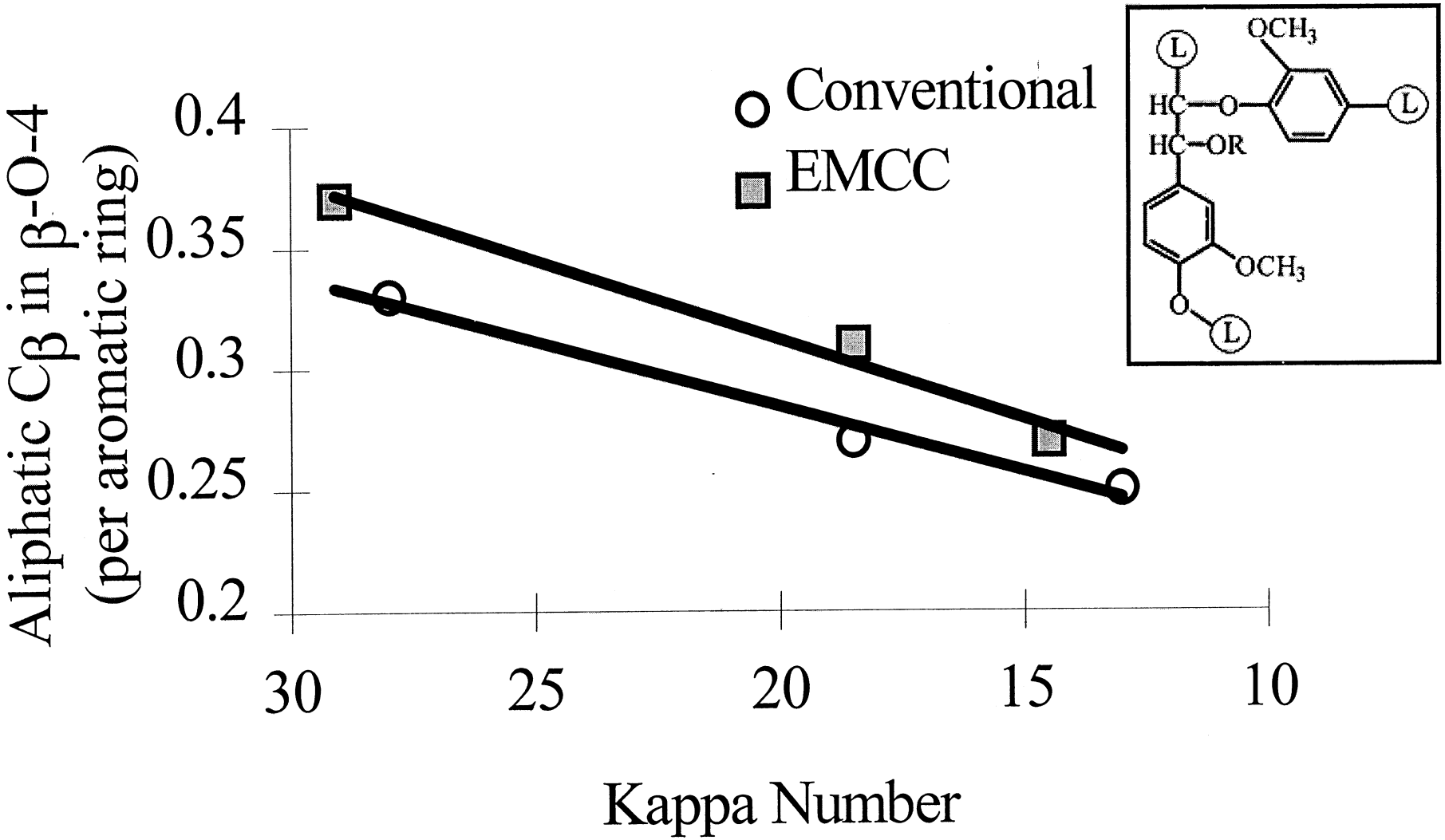
Germgard (1982)

Problem analysis



Guaiacyl phenolic content
(mmol/g)
1.4
1.3
1.2
1.1
30
25
20
15
10
Kappa number
Conventional
EMCC
L
OCH3
OH

Substituted aromatic carbons (per aromatic ring)
4.3
4.2
4.1
4
3.9
30
25
20
15
10
Kappa Number
Conventional
EMCC
OCH3
OH
L


Aliphatic Cβ in β-O-4
(per aromatic ring)
0.4
0.35
0.3
0.25
0.2
30
25
20
15
10
Kappa Number
Conventional
EMCC
OCH3
L
HC
O
HC
OR
OCH3
O
L

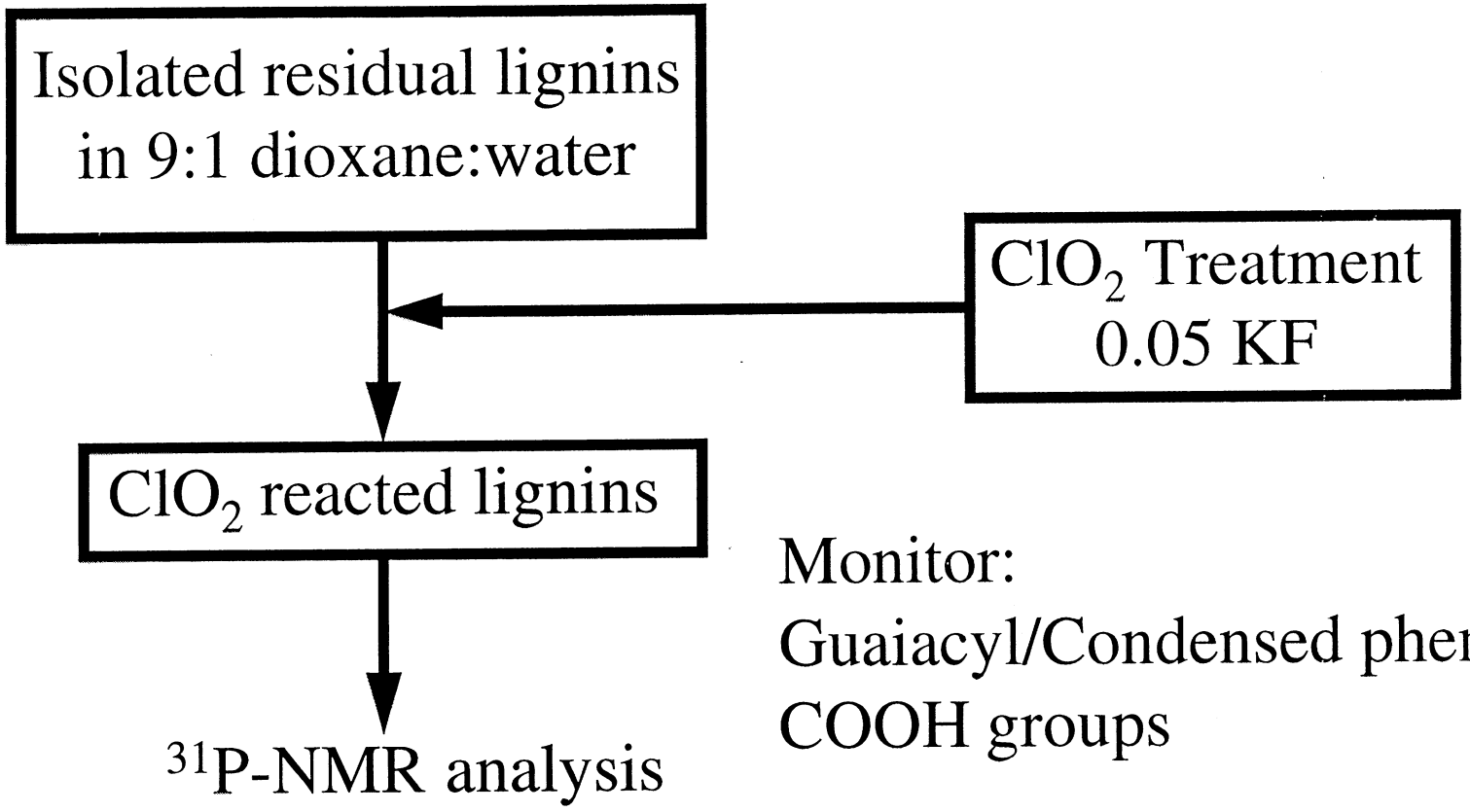
Summary of spectroscopic studies of residual lignin and relationship to pulp bleachability

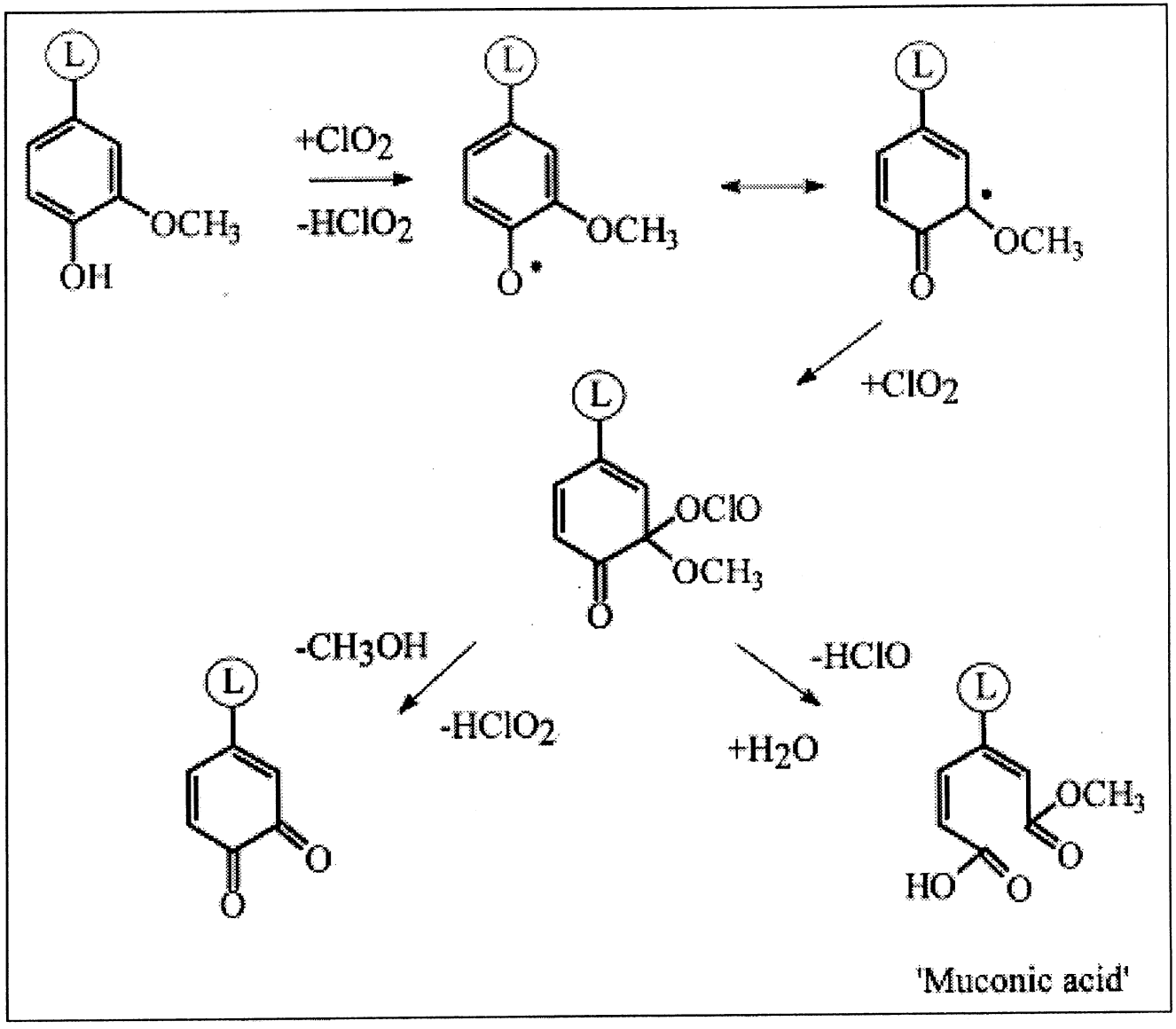
- Lower kappa number pulps are richer in phenolic content yet harder to bleach
- Positive correlation between pulp bleachability and the content of condensed structures and aryl ether linkages

Reactivity of residual lignin towards ClO_2

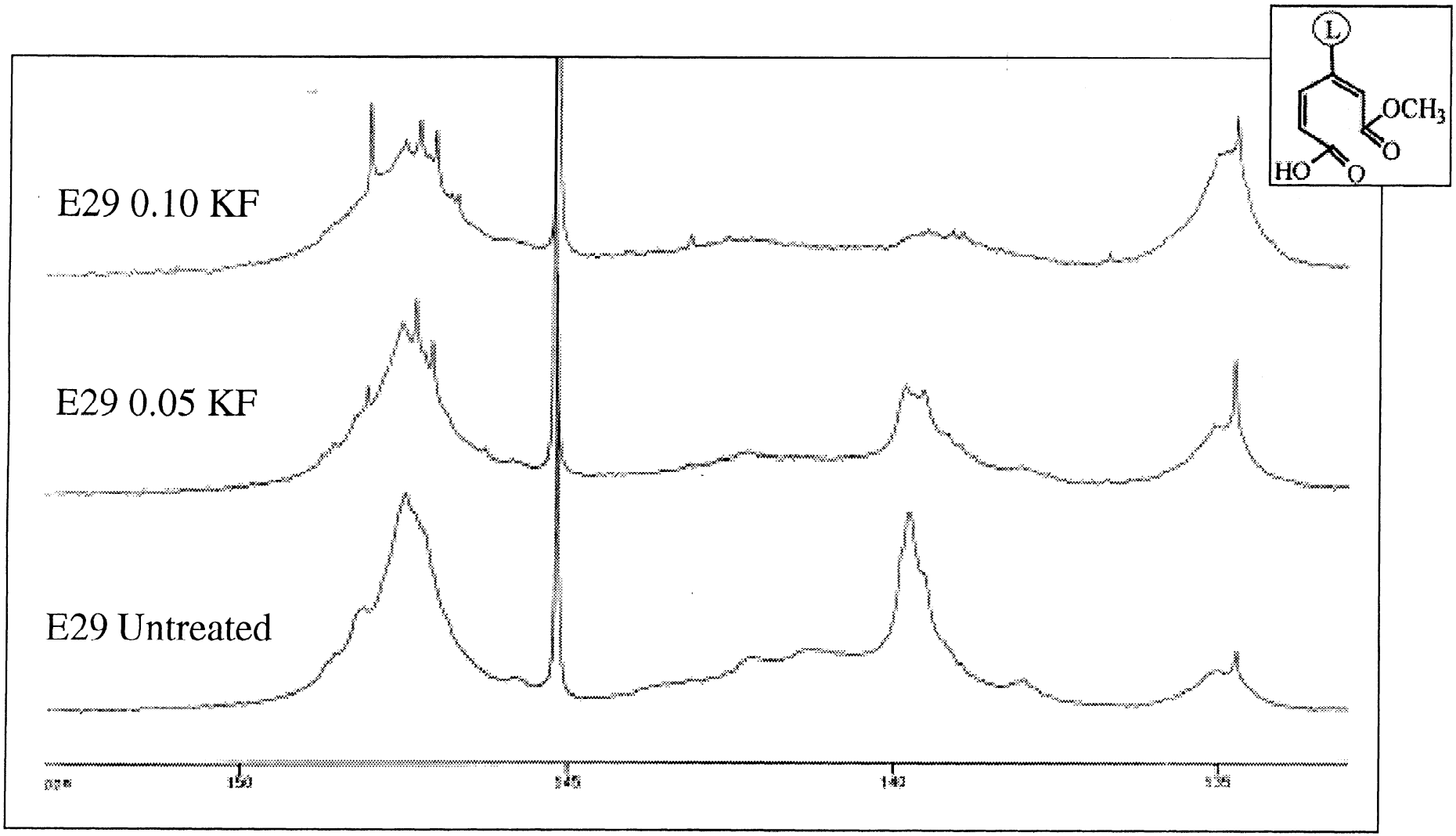
Objective: Understand the reactivity of residual lignins by treating the various isolated residual lignins with ClO_2 and monitor the functional groups changes to the lignin

Experimental




L
OCH3
OH
+ClO2
-HClO2
O
+ClO2
OClO
-CH3OH
-HClO2
-HClO
+H2O
HO
'Muconic acid'

^{31}P-NMR spectra of residual lignin treated with ClO_2



Change in functional groups (mmol/g) after ClO_2 treatment

Lignin ID	Condensed -OH	Guaiacyl -OH	COOH
C28	-0.21	-0.31	0.18
C18	-0.25	-0.32	0.14
C13	-0.26	-0.35	0.17
E29	-0.26	-0.32	0.22
E18	-0.26	-0.35	0.15
E14	-0.33	-0.41	0.14

Conclusions

- Bleachability of kraft pulps
  - higher kappa pulps are easier to delignify (lower TAC/Δ kappa)
  - E18 pulp was easier to delignify than C18 pulp
- Residual lignin structural analysis
  - higher kappa pulps are less 'condensed' and richer in aryl ether linkages
  - EK residual lignins are less 'condensed' and richer in aryl ether linkages compared to CK residual lignins at similar kappa numbers

Conclusions

- Residual lignin reactivity
  - higher kappa residual lignin was more reactive towards ClO_2
  - EK residual lignin was more reactive than CK
- Evidence supporting a relationship between residual lignin structure and bleachability

Acknowledgments

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